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AN ATTEMPT TO FIND THE AMOUNT OF PHOSPHORUS IN THREE SAMPLES OF STEEL.[1]

BY CHAS. B. DUDLEY, AND F. N. PEASE, Chemist and Assistant Chemist, Pennsylvania Railroad, Altoona, Pa.

SOMETHING over a year and a half ago, in connection with the preparation of a method for determining phosphorus in steel, to be used as a part of the specifications on which steel is bought, for the use of the Pennsylvania Railroad Company, we deemed it essential to know pretty accurately, the amount of phosphorus in each of three different samples of steel. The use made of the results finally obtained from these steels, is given in our paper, "On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method," and what follows here, is an account of the various efforts made to get the desired information. It will be observed before we have finished, that what at first seemed a very simple thing, proved in the end to be a very difficult affair, and that after all the work done on the subject, the final result is still not entirely free from doubt.

The three samples of steel were as follows: No. 1 was boiler plate made by the open hearth process, and containing presumably about 0.15 per cent. of carbon, and less than 0.05 per cent. of phosphorus. No. 2 was a piece of a locomotive driving tire, made by the open hearth process, and containing presumably from 0.50 per cent. to 0.60 per cent. of carbon and

[1] Read at the Baltimore meeting, December 28, 1893.

3-13-94

from 0.05 per cent. to 0.07 per cent. of phosphorus. No. 3 was a crucible steel billet, containing presumably from 1.00 per cent. to 1.20 per cent. of carbon and less than 0.04 per cent. of phosphorus. Quite a quantity of drillings from each of these samples was prepared, care being taken to eliminate the influence of segregation as much as possible by (1) putting the drill holes entirely through the sample, and at right angles to the line of final solidification of the metal, (2) by having the drillings as fine as they could conveniently be made, and (3) by thoroughly mixing them.

The drillings having been obtained, our first thought was that we would find out the amount of phosphorus in these steels, by analyzing them ourselves, and by asking some other chemists of recognized ability, to do the same. Accordingly a quantity of the drillings was sent to four different chemists: Mr. A. A. Blair, 406 Locust street, Phila., Dr. T. M. Drown, Mass. Inst. Tech., Boston, Prof. J. W. Langley, Case School of Applied Science, Cleveland, O., and Mr. A. S. McCreath, Harrisburg, Pa. Blair used the acetate method; Drown the molybdate-magnesia method; McCreath the acetate method; Langley both these methods, and we ourselves used the molybdate-magnesia method on all the samples, and the acetate method on the No. 2 sample. We are without information as to the exact details of the methods used by the other chemists. In our own case we used the molybdate-magnesia method, exactly as described in Fresenius' Quantitative Analysis, second American edition, John Wiley and Sons, p. 763, except that we used five grams dissolved in concentrated nitric acid, instead of aqua regia, and heated to 200° C. in an air bath, as suggested by Blair in The Chemical Analysis of Iron, second edition, p. 90, in order to destroy carbonaceous matter. In using the acetate method we proceeded exactly as described in The Chemical Analysis of Iron, by A. A. Blair, second edition, p. 81, and following. We give below the results that have been obtained on these three samples of steel, in accordance with the above, as follows:

			Steel. No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Blair			0.035	0.041	0.029
Another operator			0.035	0.047	0.027
Third operator			0.035	0.047	0.028
Drown, average of duplicates			0.037	0.050	0.030
McCreath		1	0.035	0.045	0.027
		2	0.035	0.046	0.028
Langley	Acetate method	1	0.042	0.053	0.019
	" "	2	....	....	0.020
	Another operator	1	0.042	0.050	0.019
	" "	2	0.042	0.056	0.020
Langley, molybdate magnesia			0.040	0.053	0.022
Dudley and Pease	Molybdate magnesia	1	0.041	0.056	0.033
		2	0.042	0.056	0.032
		3	0.041	0.056	0.033
	Acetate method	1	....	0.047	....
		2	....	0.046	....
		3	....	0.046	....

It will be observed that these results are hardly as satisfactory as could be desired, and that if we must know as we very greatly desired to do, within a couple of thousandths of a per cent. the amount of phosphorus actually in these steels, we were thus far without this information. The extreme variation on the No. 1 steel, is from 0.035 per cent. to 0.042 per cent. a difference of 0.007 per cent. the average of the thirteen determinations being 0.0386 per cent. On the No. 2 steel, the range is from 0.045 per cent. to 0.056 per cent. a difference of 0.011 per cent., the average of the sixteen determinations being 0.0512 per cent. On the No. 3 steel, the range is from 0.019 per cent. to 0.033 per cent., a difference of 0.014 per cent., the average of the fourteen determinations being 0.0262 per cent.

In view of these results some further study was put upon the matter. It will be observed that in our own hands, the molybdate-magnesia method, and the acetate method, do not give the same results, nor do they give the same results in the hands of Langley, and we accordingly were somewhat in doubt, as to which method gave the most reliable results. In order to locate if possible the difficulty, we examined all the residues obtained, in the course of the acetate method, and to our astonishment we found phosphorus in three different places, which we will now describe.

I. It will be remembered that after the phosphorus is separated from the bulk of the iron, by means of the basic acetate precipitate, there is quite a volume of filtrate, containing iron in the protoxide form. This filtrate was allowed to stand in the beaker for a couple of days covered, and at the end of this time, the bottom of the beaker contained quite a precipitate of apparently hydrated sesquioxide of iron, which separated on standing. This precipitate was filtered off, and dissolved in dilute nitric acid and tested with molybdate solution. In no case did we fail to get a little yellow precipitate, apparently indicating that the amount of sesquioxide of iron obtained in the solution, before the basic acetate separation is made, is not quite sufficient to, or does not succeed in carrying down all the phosphorus. The directions require that a few drops of bromine water should be added, to oxidize enough iron to combine with the phosphorus, which was carefully done in every case, but so far as these experiments go, they seem to indicate that some of the phosphorus is still left behind.

II. It will be remembered that the basic acetate precipitate, is dissolved on the filter in hydrochloric acid. In our working of the acetate method, we found in a number of cases, a slight amount of material left undissolved on the filter. On collecting the filters from a number of determinations, burning off the filters, dissolving with nitric acid, and testing with molybdate, a clear reaction for phosphorus was obtained. It should be stated that the stain left on the filter paper, after dissolving in hydrochloric acid, is not in our experience universal. Under certain conditions the basic acetate precipitate apparently goes up with greater difficulty, than with others. It is also claimed that when titanium is present in iron or steel the basic acetate precipitate usually leaves a stain on the filter.

III. The filtrate from the ammonium magnesium phosphate, which it will be remembered contains some iron, and some citric acid, was treated with dilute nitric acid and evaporated to dryness on the steam table. The residue was taken up with dilute nitric acid and treated with molybdate, and here a voluminous yellow precipitate was obtained.

These experiments seemed to indicate that, in our hands at

least, the acetate method did not give quite all the phosphorus, and helped to explain the discrepancy between the molybdate-magnesia method and the acetate method. The bulk of the yellow precipitate obtained in the three places above described, especially from the citric acid filtrate, was so considerable that it seemed almost possible to get a sufficient amount of phosphorus from it to weigh, and we accordingly made three more determinations on ten (10) grams each of the No. 2 steel, by the regular acetate method, obtaining as the average of the three 0.045 per cent. The residues from the three places above described from these thirty (30) grams of steel were all collected together and the phosphorus separated from these residues by means of molybdic acid. The yellow precipitate obtained was then treated with magnesia mixture in the regular way. The results gave a percentage of 0.0053 per cent. phosphorus, and this added to the amount obtained by the direct acetate method gave the phosphorus in the No. 2 sample 0.0503 per cent. This figure it will be observed is 0.006 per cent. less than the average which we obtained on the same sample by the regular molybdate-magnesia method.

It has generally been conceded, we think, that the molybdate-magnesia method for determining phosphorus, following Fresenius, is liable to give rather high results, especially if arsenic is present and is not separated, which we did not do. We did separate the possible traces of silica from the magnesium pyrophosphate as Fresenius recommends. We were therefore still in doubt as to the amount of phosphorus in these steels, and did not feel satisfied to use any of the results obtained.

The question therefore arose with renewed force, how shall we find out how much phosphorus these three steels contain? After considerable study and discussion, the following method was decided on, namely: Start with ten grams, and proceed exactly as described in The Chemical Analysis of Iron and Steel, above mentioned, up to the point of adding the bromine. Then instead of adding a few drops, add enough bromine water to convert half a gram of the iron into the sesquioxide. Then make the basic acetate separation as described, except on account of the large amount of iron, a little ammonium acetate is

added. Dissolve the basic acetate precipitate in moderately strong hydrochloric acid, and evaporate the liquid to dryness, to render any silica present insoluble. Take up with forty cc. of strong nitric acid, and evaporate to dryness a second time, to remove the hydrochloric. Then take up with seventy-five cc. of dilute nitric acid, 1.13 sp. gr., filter, and precipitate with seventy-five cc. of molybdate mixture, with the proper precautions of the molybdate-magnesia method as to temperature and time. Collect the yellow precipitate on a filter, and after thorough washing dissolve in $2\frac{1}{2}$ cc. of strong ammonia diluted with water, and wash thoroughly with water until the total volume of solution amounts to about 100 cc. Pass hydrogen sulphide until this solution becomes dark red in color. The hydrogen sulphide readily converts the molybdic acid into molybdenum sulphide, in ammoniacal solution, and if the gas has been passed long enough, a complete separation of the molybdic acid results when the solution is treated with hydrochloric acid in slight excess. Filter off from the molybdenum sulphide, wash thoroughly with water containing a little hydrochloric acid, and evaporate nearly to dryness, in order to have controllable bulk of solution. Then take up with a little water, to which two or three cc. of dilute hydrochloric acid has been added, and filter if necessary to remove separated sulphur and a trace of molybdenum sulphide which may separate during the evaporation. Concentrate the filtrate to about fifteen cc., and add five cc. of magnesia mixture, and a little ammonia. The total volume of the solution should not now exceed twenty-five or thirty cc. The ammonium magnesium phosphate from this point is treated in the regular way.

The three samples of steel above referred to treated in this way, gave the following figures:

		No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Phosphorus	1	0.040	0.053	0.032
	2	0.040	0.054	0.033

Unfortunately the separated oxide of iron from the filtrates in the basic acetate separation, in the cases of these determinations were not examined, but subsequent examinations of this material on other samples has shown that half a gram of iron

carries down all the phosphorus, or possibly all but the merest trace. Also in the case above mentioned, nothing was left on the filter when dissolving the basic acetate in hydrochloric acid. An examination of the filtrate from the magnesium phosphate precipitate in no case failed to show a slight yellow precipitate, and these results have been confirmed by quite a number of subsequent examinations. The amount of this, however, is very slight, the bulk of the yellow precipitate obtained being very much less than is shown in the citric acid filtrate when the acetate method is used. It seems probable therefore, that notwithstanding all the precautions involved in the method described above, the results given are still a trifle low. These figures were, however, taken as representing the phosphorus content of these three samples of steel.

The method finally used on these steels, and whose results we regard as the most reliable, will be at once recognized as a modification of the combination method, first proposed by Riley, and subsequently described in detail by J. Lawrence Smith in the *American Journal of Science*, **123,** 316. This combination method seems to have several advantages and perhaps to unite, in a sense at least, the best features of the acetate and the molybdate-magnesia methods. The acetate method is used to concentrate the phosphorus from a large amount of material, into a very small amount of iron. The molybdate method is used to separate the phosphorus from the iron. The conversion of the molybdic acid into sulphide in ammoniacal solution is due to a suggestion of Hundeshagen. It will be observed that by the method as we actually used it there are two opportunities to get rid of arsenic, *viz.*, before the basic acetate precipitation is made, and also along with the molybdenum sulphide. Subsequent experiments seemed to indicate that the first of these two separations can be omitted with safety. The method is long and laborious, but seems to offer, all things considered, perhaps the most accurate means now known of determining small amounts of phosphorus in steel. It may be well to add that on coming subsequently to determine phosphorus in these three steels by the volumetric method, a difficulty was found with the No. 2 steel. This will appear by a comparison of the

results obtained on the three steels by the two methods, as follows:

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.
Combination method	0.040	0.053	0.032
Volumetric method	0.040	0.059	0.032

In view of this discrepancy an arsenic determination was made on the No. 2 steel, following exactly the method described in The Chemical Analysis of Iron, p. 188, except that we started with fifty grams. The result obtained was

	No. 2. Per cent.
Arsenic	0.009

This result seems to indicate that arsenic is the cause of the discrepancy in the No. 2 steel, and apparently confirms again the view that arsenic interferes with the determination of phosphorus by means of molybdic acid.

It is perhaps not essential but may not be amiss to say that where the amount of phosphorus is large a difficulty may arise with the combination method, if ten grams are used to start with, due to the large bulk of molybdenum sulphide obtained. Very large amounts of molybdenum sulphide are difficult to wash clean. Of course the difficulty is easily overcome by starting with less than ten grams.

ON SOME POINTS IN THE DETERMINATION OF PHOSPHORUS IN STEEL BY THE VOLUMETRIC METHOD.[1]

By Chas. B. Dudley and F. N. Pease, Chemist and Assistant Chemist, Pennsylvania Railroad, Altoona, Pa.

ONE of the most common methods of separating phosphorus from iron, either in ores, pig iron, wrought iron or steel, is by means of molybdic acid, the separation giving rise to the well-known yellow precipitate of ammonium phosphomolybdate. The subsequent treatment of this yellow precipitate is very varied. Some chemists prefer to dissolve the precipitate in ammonia, and then determine the phosphoric acid by means of magnesia mixture. Others prefer to weigh the yellow precipitate just as obtained, and some even to measure the volume of

[1] Read at the Baltimore meeting, December 28, 1893.

this yellow precipitate in a specially graduated apparatus. Perhaps however, by far the largest number of chemists, prefer to treat the yellow precipitate by some volumetric method, either what may be called the alkali method, described by Handy in the *Proceedings of the Engineer's Society of Western Penna.*, **8,** 78, or the perhaps better known permanganate method, described by Emmerton, published in the *Trans. A. I. M. E.*, **15,** 93, and subsequently modified by Wood, Shimer, Drown, Jones, and others. We use the permanganate method. This method as we prefer to use it, and with all the precautions which we deem essential to secure uniform and accurate results, except as to the interference produced by arsenic, has been published in the *J. Anal. Appl. Chem.*, **7,** 108, and also in the *J. Am. Chem. Soc.* **15,** 519. What follows is a discussion of some points suggested by the work done preliminary to drawing up the method above referred to.

In order that what is given may be clearly understood, it may not be amiss to state that by this method, the steel is dissolved in nitric acid of 1.13 sp. gr., the solution boiled a few seconds, and then treated with potassium permanganate to destroy carbonaceous matter, and possibly secure complete oxidation of the phosphorus; the separated manganese oxide, reduced by a few crumbs of ferrous sulphate, the solution then heated to a definite temperature, and a measured volume of molybdate solution, which is likewise at a definite temperature, added, the vessel enclosed to prevent loss of heat, and shaken vigorously for five minutes, allowed to stand a few minutes for the precipitate to settle, and then filtered. After thorough washing with acid ammonium sulphate wash water, the yellow precipitate is dissolved in ammonia, the solution treated with a definite amount of sulphuric acid, and then passed through the reductor, and finally titrated with potassium permanganate of known strength, the amount of phosphorus being ultimately obtained by multiplying the number of cubic centimeters of permanganate used by the proper factor.

It is obvious that the accuracy of the determination by the method briefly outlined above, depends on several conditions:

I. Is all the phosphorus in the steel taken to start with

actually in the yellow precipitate obtained, or in other words, can phosphorus be completely separated from iron by molybdic acid? Upon this point we have done no work, and cannot express an opinion. The late J. Lawrence Smith used to claim that the complete separation of very small amounts of phosphorus from large amounts of iron by means of molybdic acid was at least doubtful, and that the most reliable procedure consisted in first concentrating the phosphorus into a very small amount of iron, and then separating it from this iron by means of molybdic acid. Assuming, however, that all the phosphorus in the steel is in the yellow precipitate, several further questions arise.

II. Is the yellow precipitate of constant composition, that is, is it independent of the conditions under which it is formed? It is obvious that this is a very important point for all those methods which either weigh or measure the yellow precipitate, and also for the permanganate volumetric method, which in reality actually measures not the phosphorus or phosphoric acid in the yellow precipitate but rather the molybdic acid, the phosphorus being determined from its relation to the molybdic acid. If now the yellow precipitate is not of constant composition, or more definitely if the relation between the phosphorus and molybdic acid in this precipitate is not a constant one, but is affected by the conditions under which the precipitate is formed, it is clear that these conditions must be definitely defined, and always closely followed, or there will be great uncertainty in the results. What then are the facts in the case? It is well known that almost from the beginning of the use of molybdic acid in phosphorus determinations there has been more or less uncertainty as to the constitution of the yellow precipitate, and especially that, depending on the conditions, it is very liable to be contaminated with free molybdic acid. Furthermore, Emmerton has apparently demonstrated in the place cited above, that the temperature of precipitation has a very important influence on the final result. He also claims that the amount of free acid in the solution, the concentration of the solution, and the length of time allowed for precipitation also affect the final result. Other workers, especially Wood, in the

J. Anal. Chem., **1**, 138, Shimer, *Trans. A. I. M. E.*, **17**, 100, and Drown, *Trans. A. I. M. E.*, **18**, 90, have put a good deal of study on the method. None of the determinations given that we have been able to study, show that the final result is independent of the conditions under which the yellow precipitate is obtained. We ourselves have made a good many experiments, varying the conditions under which the yellow precipitate is obtained, and feel safe in saying that almost any variation in the conditions will produce some difference in the final result. Much of our work simply confirms that of other operators. Perhaps it would be worth while to give a single illustration.

Two sets of one gram each of three samples of steel containing different amounts of carbon and phosphorus were dissolved in seventy-five cc. of 1.13 sp. gr. nitric acid, and further treated exactly alike according to our standard method above referred to, except that before adding the molybdate solution, ten cc. of strong ammonia was added to each flask of one set. This procedure would as is evident, result in the formation of the yellow precipitate in one set in a menstruum containing more ammonium nitrate, and less free nitric acid than the other contained. The results obtained are as follows, the figures being the phosphorus in the three steels:

		No. 1 steel. Per cent.	No. 2 steel. Per cent.	No. 3 steel. Per cent.
Without ammonia	1	0.036	0.055	0.029
	2	0.037	0.055	0.029
	3	0.037	0.055	0.030
With ammonia	1	0.047	0.064	0.036
	2	0.043	0.062	0.033
	3	0.045	0.067	0.039

The difference in the results is quite marked. Diminution in free acid and increase in ammonium nitrate apparently leads to higher figures and less uniformity in duplicate determinations. Some of our experiments indicate that even a much less change in the proportions of free acid and ammonium nitrate than given above affects the final result. Also that in addition to the variables mentioned above, a different result is obtained when sugar or other organic substance is used to reduce the separated manganese oxide than is given when ferrous sulphate

is used. Finally there are quite strong indications, that the total amount of molybdic acid present in the solution and even its state of oxidation have an influence on the final figures obtained.

If it be allowed then that the conditions, under which the yellow precipitate is formed affect its constitution, or more definitely, affect the ratio between the molybdenum and phosphorus in this precipitate, or what amounts to the same thing, affect the final result, two things are evident.

1. In order to secure accurate and concordant results, it is necessary that the conditions under which the yellow precipitate is obtained shall be very clearly and sharply defined, and that on making the analyses, these conditions shall be very rigidly maintained.

2. It will not do to use ratios based on the analysis of the yellow precipitate obtained under one set of conditions as a means of calculation for precipitates obtained under another and different set of conditions.

As an example of this second statement, it seems clear, if the preceding views are correct, that if a chemist obtains a quantity of the yellow precipitate from sodium phosphate with no iron present, and the conditions entirely different from those which prevail in the determination of phosphorus in steel, and then makes an analysis of this yellow precipitate to determine the ratio between molybdic acid and phosphorus, although the figures he obtains may be quite accurate, he is still not at liberty to use these figures in determining phosphorus in iron and steel and claim that they give accurate results. It is of course conceded that they may be accurate but there is no certainty of this. It should be stated that the amount of phosphorus in the yellow precipitate is so small, and the amount of molybdic acid is so large, that there is room for considerable variation in ratios without giving rise to very serious differences in results, especially in steels low in phosphorus. This fact may help to account for the claim so generally made by different chemists that their results agree within reasonable limits of error with those of other good chemists. But if it is desired to obtain fairly accurate and concordant results, we see no way of escaping from the two statements given above.

If these points be conceded it is obvious that a still further very important question arises, *viz.*:

III. How shall the proper factor for use with the permanganate of potash be obtained? It is clear, since the permanganate of potash solution is standardized against metallic iron, that we need two ratios, first, the ratio between molybdic acid and iron, and second, the ratio between molybdic acid and phosphorus in the yellow precipitate obtained under definite conditions. What then are these ratios? On looking over the literature on the subject, we find two or three serious uncertainties. The ratio between iron and molybdic acid is evidently affected by the change which takes place in the molybdic acid when it passes through the reductor, and we do not find that there is agreement between those who have worked on this point. Furthermore, Jones has apparently shown in the *Trans. A. I. M. E.*, **18**, 705, that the use of the reductor gives different results than are obtained when the molybdic acid in the yellow precipitate is reduced by granulated zinc in a beaker as originally proposed by Emmerton. Again the published ratios between molybdic acid and phosphorus, vary between 100 : 1.54 and 100 : 1.90 if we may use our own figures for illustration. It is clear therefore that there are two difficulties in the way of using any of the published ratios, first, which ratios shall be used, and second, the point already discussed quite at length, that these ratios vary, or at least the final results vary according to the conditions under which the yellow precipitate is obtained.

Two methods of procedure are clearly open to us.

First, obtain a quantity of the yellow precipitate under the conditions which we deem essential, and then make independent determinations of the phosphorus and molybdic acid in this precipitate. This would give the ratio between these two constituents. Then pass a quantity of the same precipitate through the reductor and titrate with permanganate. This will give the ratio between molybdic acid and iron. This we have not done yet, partly for lack of time and partly from the difficulties of the analysis. In our experience it is not easy to dry and weigh the yellow precipitate without its undergoing change in the process, and our experience with methods of determining

molybdic acid is also meager. There is need of some good and careful work on this point.

In view of these uncertainties, we chose the other method of procedure, *viz.:*

Second, determine the phosphorus in several samples of steel by the most accurate known gravimetric method, then make an analysis for phosphorus in these same steels by the volumetric method, and then use such a factor with the potassium permanganate as will bring these results together. The work done on the steels chosen for this purpose is given in our paper "On an Attempt to Find the Amount of Phosphorus in Three Samples of Steel."

It is evident that this procedure, while it enables us to get a factor to use with the potassium permanganate in the phosphorus determinations by the volumetric method as we use it, does not throw any light on the ratios between iron and molybdic acid, and between molybdic acid and phosphorus in the yellow precipitate as we obtain it. But if we assume that the ratio of iron to molybdic acid is 100 : 90.76 it follows that the ratio of molybdic acid to phosphorus in the yellow precipitate as we obtain it is 100 : 1.90 and this is the calculation which we have used in our published volumetric method above referred to.

One further question may arise, *viz.:* In view of the apparent variability of the yellow precipitate according to the conditions under which it is obtained,

IV. If the conditions are made constant, will the results obtained be uniform and agree with each other?

In reply to this we may say that so far as our experience has gone, the agreement between duplicate determinations on the same sample of steel where the conditions of the method as published are rigidly adhered to, rarely exceeds more than a couple of thousandths of a per cent., also different operators using the published method on the same sample of steel, after a little experience is obtained with it, rarely disagree more than three or four thousandths.

THE EXACT DETERMINATION OF PHOSPHORUS BY THE MOLYBDATE METHOD IN IRON, STEEL, AND ORES, WHICH CONTAIN ARSENIC.[1]

By James O. Handy, Chemist of The Pittsburgh Testing Laboratory, L'td.

CLASSIFICATION OF EXISTING METHODS FOR PHOSPHORUS.

1. The acetate method of Blair and others.
2. The molybdate methods.

(a) Methods in which the phosphomolybdate is weighed (methods of E. F. Wood and others).

(b) Methods in which the amount of yellow precipitate is estimated volumetrically.

(a′) By permanganate (methods of Emmerton, Drown, Jones, and others).

(b′) By alkali (methods of Manby, Handy, and others).

3. The combination methods.

(a) The acetate and molybdate methods.

(b) The molybdate and magnesia methods.

In the "acetate" methods the phosphorus is precipitated as phosphate, after separating by hydrogen sulphide, any arsenic which is present. The methods are long and the manipulation difficult.

In the "molybdate" methods, the phosphorus is precipitated as ammonium phosphomolybdate and weighed or titrated. Arsenic, which is believed to be of rare occurrence, is disregarded. It is, however, a fact, that, when arsenic is present in a solution from which phosphorus is precipitated as phosphomolybdate, a portion of the arsenic accompanies and contaminates the phosphorus precipitate.

The "molybdate" methods are in general, very short and their manipulation simple; they are widely used. With the drawback of arsenic interference removed, the molybdate method takes front rank for simplicity, brevity and accuracy.

[1] Read at the Baltimore meeting, December 28, 1893.

TABLE I.

EXTENT OF THE INTERFERENCE OF ARSENIC IN PHOSPHORUS DETERMINATIONS.

Substance analyzed.	Phosphorus per cent. contained.	Arsenic per cent. contained.	Method.	Temperature of precipitation.	Apparent per cent. phosphorus.	Error caused by arsenic.	Remarks.
Steel	0.096	0.050	J. O. Handy	85° C.	0.094	None	Within limit of error
"	0.096	0.050	"	"	0.095	"	"
"	0.098	0.100	"	"	0.098	"	"
"	0.098	0.100	"	"	0.099	" to 0.001	"
"	0.096	0.250	"	"	0.099	0.003	
"	0.096	0.350	"	"	0.102	0.006	
"	0.096	0.500	"	"	0.106	0.010	
"	0.096	0.750	"	"	0.111	0.015	
"	0.096	1.870	"	"	0.125	0.029	
"	0.012	0.100	"	"	0.012	"	"
"	0.012	0.500	"	"	0.011	"	"
"	0.012	1.000	"	"	0.011	"	"
Pig iron	0.036	0.100	"	"	0.039	0.003	
" "	0.036	0.150	"	"	0.043	0.007	
" "	0.083	0.100	"	"	0.088	0.005	
" "	0.083	0.150	"	"	0.094	0.011	
" "	0.297	0.500	" and we'h'g	"	0.315	0.018	
Ferro-mang'se	0.292	0.500	evaporat'n, neutraliz'n, weighing	"	0.313	0.021	
Iron ore	0.096	0.500	"	"	0.135	0.038	
Mang'se ore	0.212	0.500	"	"	0.264	0.052	

EXPERIMENTS PROVING THAT ARSENIC DOES NOT PRECIPITATE WHEN LITTLE OR NO PHOSPHORUS IS PRESENT.

Experiments.—Two grams of magnetic iron ore, (a very pure concentrate), showed 0.002 per cent. phosphorus. A duplicate containing 0.500 per cent. of arsenic, in the fully oxidized form, showed also exactly 0.002 per cent. of phosphorus.

The filtrate, which contained arsenic, was heated for a short time to 60°–70° C. before molybdic acid or arsenomolybdate began to separate. The same result was repeatedly obtained with arsenical filtrates from phosphomolybdate precipitates.

A solution of arsenic acid in nitric acid, properly prepared as for phosphorus determination gives no precipitate at 85° C. with molybdate solution unless the heating is continued.

The experiments described prove very clearly that the precipitation of arsenic with phosphomolybdate is a mechanical one; that the arsenic is only *dragged* down. With little or no phosphorus, no arsenic precipitates.

The case is parallel to the contamination of the first ferric

hydroxide precipitate, with lime, or of the first oxalate of lime precipitate, with magnesia.

In these cases, solution and re-precipitation of the contaminated precipitates, effects their purification.

Experiments (Table II) prove that the same treatment, properly applied, is equally efficient in purifying arsenical phosphomolybdate.

The exact method of procedure follows:

TABLE II.

ELIMINATION OF ARSENIC FROM PHOSPHOMOLYBDATE.

Substance analyzed.	Phosphorus contained.	Arsenic contained.	Method.	Temperature of precipitation.		Phosphorus found.	Error.
				First	Second		
Steel	0.096	0.500	J. O. Handy	80° C.	75° C.	0.096	none
"	0.096	0.500	"	"	"	0.096	"
"	0.096	0.500	"	"	"	0.097	0.001
"	0.096	1.000	"	"	"	0.097	0.001
"	0.096	none	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.095	0.001
"	0.096	"	"	"	"	0.094	0.002
"	0.096	0.500	"	85° C.	85° C.	0.097	0.001
"	0.096	0.500	"	"	80° C.	0.094	0.002
"	0.038	0.500	"	80° C.	75° C.	0.036	0.002
"	0.038	0.500	"	"	"	0.037	0.001
"	0.038	0.500	"	"	"	0.039	0.001
"	0.038	none	"	"	"	0.037	0.001
Pig iron	0.082	0.500	"	"	"	0.081	0.001
" "	0.082	0.500	"	"	"	0.081	0.001
Ferro-mang'se	0.282	0.500	evaporat'g / weighing	85° C.	75° C.	0.281	0.001
Pig iron	0.286*	0.500	J. O. H. and "	"	"	0.289	0.003*
Iron ore	0.083	0.500	Evap. " "	"	"	0.085	0.002
Manganese	0.199	0.500	" " "	"	"	0.200	0.001

* NOTE.—A little lost.

THE METHOD OF REDISSOLVING THE PHOSPHOMOLYBDATE AND FREEING IT FROM ARSENIC.

Having separated the phosphorus as phosphomolybdate by any good method and washed it well with one per cent. nitric acid, place a twelve ounce Erlenmeyer flask under the funnel.

Dissolve the yellow precipitate by ammonium hydroxide wash (1 : 6), using about fifteen cc. in all, and wash it into the flask. Dilute the solution to about seventy-five cc. and heat to 75° C. and add a mixture of ten cc. HNO_3 (1.42) and twenty-five cc. of molybdate solution (E. F. Wood's formula), shake well, filter and wash

(a) with one per cent. nitric acid, dry and weigh, or

(b) with one per cent. nitric acid and $\frac{1}{10}$ per cent. potassium nitrate, dissolve and titrate (Handy's method).

The greater part of the analytical work of this paper has been done by my assistant Mr. Geo. O. Loeffler.

METHODS USED.

For Steel and Pig-iron.—The method used in all analyses of steel and pig-iron, was the one published by the author in 1892 (*Trans. Engineer's Society of Western Pennsylvania* March, *1892*, and *J. Anal. Appl. Chem.*, April, *1892*).

For Ferromanganese.—Two grams, dissolved in nitric acid, (1.42), and the solution evaporated to dryness. The residue, having been redissolved in hydrochloric acid, (1.20) the solution was diluted and filtered. The filtrate was treated with ammonium hydroxide till ammoniacal, then acidified with nitric acid, heated to 85° C. and precipitated with fifty cc. of molybdate solution.

For Iron and Manganese Ores.—Two grams dissolved in aqua regia (five per cent. HNO_3(1.42) and ninety-five per cent. HCl (1.20), and the solution evaporated to dryness. Subsequent procedure was as described above for ferromanganese after the evaporation. Phosphorus, in "insoluble residues" was separated and determined.

Arsenic was added as dry As_2O_3 to the samples when weighed out. The reagents used in the analysis oxidized it to arsenic oxide.

NOTES AND QUERIES ON DR. DUDLEY'S METHOD OF DETERMINING PHOSPHORUS IN STEEL.

By O. S. Doolittle, Chemist, and Alban Eavenson, Assistant Chemist Philadelphia and Reading Railroad Company.

Received February 10, 1894.

THE object of the work outlined in this paper was to ascertain the accuracy of the method proposed by Dr. Dudley for the volumetric analysis of phosphorus in steel, described in *J. Am. Chem. Soc.*, Sept., *1893*, p. 519, and to determine if a separation of phosphorus could be made in the presence of arsenic with a sufficient degree of accuracy for commercial purposes

by this method or any modification of it.

Our first undertaking was to ascertain if the new ratio between phosphorus and molybdic acid in the yellow precipitate of 1.90, brought forward by Dr. Dudley, was correct. The commonly accepted factor as found by Emmerton and others is 1.794, *Trans. A. I. M. E.*, **15,** 93, R. Finkener, *Ber. d. chem. Ges.*, **11,** 1638, Henry Pemberton, *Chem. News*, **46,** 4, Von der Pfordten, *Ztschr. anal. Chem.*, **23,** 422, and very recent work by H. C. Babbitt, *J. Anal. Appl. Chem.*, **7,** 165, has confirmed this ratio. However, as Dr. Dudley used an entirely different method for determining this ratio, we have followed as nearly as possible his work as outlined in the *American Engineer and Railroad Journal*, Jan. *1893*, p. 18, but have been wholly unable to obtain his figure.

Determination of the Ratio between Phosphorus and Molybdic Acid in the Yellow Precipitate.—Four samples of steel of very different carbon composition were taken, and the phosphorus determined both gravimetrically and volumetrically in each, and from the figures obtained, the ratio between the phosphorus and the molybdic acid in the yellow precipitate, formed in the volumetric analysis under the conditions used, was computed. The complete analyses of the steel used in this and subsequent investigations are as follows:

	Carbon, per cent.	Manganese, per cent.	Silicon, per cent.	Gravimetric phosphorus, per cent.	Sulphur, per cent.
No. 27	0.188	0.321	0.020	0.110	0.052
No. 789	0.997	0.427	0.226	0.021	0.024
No. 344	0.588	1.295	0.079	0.065	0.107
No. 65	0.166	0.577	0.072	0.012	0.025

For our gravimetric determination we used the combination method as described by Dr. Dudley. The acetate method was followed up to the point of obtaining the basic acetate precipitate, at which stage enough bromine water was added to oxidize fully one-half a gram of iron, and the solution boiled. It was then cooled down and the acetate precipitation made exactly as described in Chemical Analysis of Iron, by A. A. Blair. This precipitate was dissolved in hydrochloric acid, and all traces of iron washed from the paper. After expelling the hydrochloric acid from the filtrate by repeated evaporations with nitric acid, seventy-five cc. of nitric acid 1.135 sp. gr. were added, the solu-

tion boiled, oxidized with potassium permanganate, and reduced with ferrous sulphate, as described in Dr. Dudley's routine method. The solution at 85° C. was then treated with seventy-five cc. of molybdic acid at 27° C., the yellow precipitate shaken down, filtered and washed free of molybdic acid. We test for the presence of molybdic acid as follows: About four cc. of the acid wash water are caught in a test tube as they run through the filter, and treated with a few drops of dilute ammonium sulphide. The least presence of molybdic acid will cause the liquid to darken slightly. The cloud of sulphur produced by the addition of ammonium sulphide to the acid solution does not interfere in any way with the delicacy of the test. We have found this test far more sensitive than the one used by Dr. Dudley, who allows the acid wash water to drop into a dilute solution of ammonium sulphide, the test thus being in the alkaline solution. We have frequently found yellow precipitates which according to the alkaline solution test were thoroughly washed, yet with the acid test show unmistakable signs of molybdic acid which required one or two more washings to remove. The yellow precipitate was then dissolved in ammonia and saturated while warm with hydrogen sulphide, and the red solution of molybdenum sulphide slightly acidified with hydrochloric acid. The precipitate of molybdenum sulphide was allowed to settle, then filtered off rapidly on a large folded filter, avoiding contact with the air as much as possible, and washed thoroughly with strong hydrogen sulphide water containing a little hydrochloric acid. The large filtrate was then evaporated, and on boiling, it was invariably found that a small amount of molybdenum sulphide separated out. This was filtered off and the resulting filtrate concentrated to a bulk of about four cc. The phosphorus was then precipitated with from five to eight cc. of magnesia mixture and a small amount of ammonium hydroxide, the cold solution being vigorously stirred until precipitation began, when ammonium hydroxide amounting to one-third of the bulk of the solution was added, and the analysis allowed to stand for twelve hours. The precipitate was then filtered off, washed with ammonium nitrate until free from chlorine, and ignited. This precipitate was invariably contaminated with molybdic acid. It

was purified by dissolving in hot dilute hydrochloric acid, filtering, evaporating the filtrate to a small bulk, and precipitating as before. For our volumetric determination of the phosphorus in these samples we followed the preceding method up to the point of obtaining the ammoniacal solution of the yellow precipitate. This solution was acidified with sulphuric acid, passed through the reductor and titrated with permanganate, one cc. of which equals 0.003350 grams iron, and assuming as Dr. Dudley has, that the ratio between iron and molybdic acid is 90.76, the commonly accepted factor, we obtain the results in the table below.

	Permanganate used by volumetric method, cubic centimeters.	Phosphorus by gravimetric method, per cent.	Ratio between phosphorus and molybdic acid.	Error in ratio for each 0.001 per cent. error in gravimetric determination.
No. 27	103.1	0.110	1 : 1.759	0.016
" 789	19.0	0.021	1 : 1.826	0.087
" 344	59.4	0.065	1 : 1.813	0.027
" 65	11.2	0.012	1 : 1.806	0.151

A glance at the ratios obtained between phosphorus and molybdic acid in the above table will show that they are very irregular, but this will be explained by the last column of figures which point out that the gravimetric determinations of phosphorus must be made with absolute accuracy in order to have these ratios agree. The only point we wish to call attention to in the above table of ratios is the fact that they are all much lower than the ratio 1.90 proposed by Dr. Dudley, and obtained by him in a similar manner.

Not satisfied with the above results, we turned our attention to the actual analysis of the yellow precipitate, which was prepared for our investigations as follows: To a solution of ferric nitrate in nitric acid of 1.135 sp. gr., was added a sufficient amount of phosphoric acid to make the solution correspond to that of a steel containing about one per cent. of phosphorus. The yellow precipitate was shaken down from this, exactly in accordance with Dr. Dudley's method of phosphorus analysis. It was washed by decantation with ammonium sulphate, then with water, and finally dried to a constant weight at 130° C. This precipitate was found to be so hygroscopic that it was practically impossible to obtain accurate weights of it for analy-

sis. To avoid this difficulty, after carefully weighing it, the entire precipitate was dissolved in a slight excess of ammonium hydroxide, filtered through a balanced filter paper into a tared 200 cc. flask, the filter being washed with water until the 200 cc. mark was reached. The small amount of insoluble matter on the filter was determined after drying at 100° C., and the weight deducted from the original weight of the yellow precipitate. We now have a known weight of yellow precipitate in a known weight of solution, successive portions of which were weighed out from time to time for the determination of phosphorus and molybdic acid.

Phosphorus in Yellow Precipitate.—This was determined as follows: Accurately weigh off about twenty-five grams of solution, which is equivalent to about one gram of yellow precipitate, add ten cc. of magnesia mixture, stir well until precipitation begins, then add ammonium hydroxide to the amount of about one-third the bulk of the original solution, and allow to stand for several hours. Filter and wash with ammonium nitrate solution until free from chlorine, then ignite while moist. Purify the magnesium pyrophosphate by dissolving in dilute hydrochloric acid, filtering from any insoluble residue, and precipitating as before by the addition of ammonium hydroxide, five cc. of ammonium chloride solution, and five cc. of magnesium mixture. Allow to stand twelve hours, ignite and weigh.

The reagents used were made up as follows:

Ammonium chloride.—One part ammonium chloride to eight parts of water.

Magnesia mixture.—From magnesium chloride as per Chemical Analysis of Iron, p. 58, by A. A. Blair.

Ammonium hydroxide.—0.90 sp. gr.

Ammonium nitrate wash water.—One part ammonium hydroxide 0.90 sp. gr. to three parts water, then add two grams of ammonium nitrate for each 100 cc. of solution.

Molybdic Acid in Yellow Precipitate.—The method used for this determination was as follows: Weigh off accurately an amount of solution equivalent to about 0.25 gram of yellow precipitate, dilute with 150 cc. of water and bring to a boil. Neutralize the boiling solution with acetic acid, and add about five cc. in excess of the neutral point. Add at once twenty-five cc. of lead acetate,

or one cc. for every 0.01 gram of yellow precipitate present in the solution, and allow to digest an hour and a half at nearly a boiling temperature, in order to render the precipitate compact and granular. Filter on a Gooch crucible and wash with hot water about eight times by decantation. After the fifth or sixth washing the filtrate should give no reaction for lead when tested with ammonium sulphide. Dry to a constant weight at 130° C. This gives us the weight of $Pb_3(PO4)_2 + PbMoO_4$. From the previous determination of phosphorus we now compute the $Pb_3(PO4)_2$, and deduct this weight from that of the mixed precipitates. The difference gives us the weight of $PbMoO_4$, which multiplied by the factor 0.39237 equals molybdic acid (MoO_3).

The reagents used were made up as follows:

Lead Acetate.—Sixty grams crystallized salt in two liters of water, to which fifteen cc. of acetic acid were added.

Acetic Acid.—1.04 specific gravity.

Before using the above method for the determination of molybdic acid, we carefully investigated its merits and found it to be thoroughly reliable under all ordinary conditions of precipitation, the acidity, bulk and temperature of the solution having only a slight influence. On attempting to ignite the precipitate, however, as directed in the method as originally published in the *Ber. d. chem. Ges.*, **4**, 280, we invariably found a loss varying from 0.2 per cent. to 3.0 per cent., and even more, according to the duration and intensity of ignition. But by drying on a Gooch crucible at 130° C. we obtained very constant results, which we believe to be in every way reliable.

The analysis of the yellow precipitate by the above methods gave us as follows: Phosphorus, 1.648 and 1.644 per cent., an average of 1.646 per cent.

Molybdic acid, 91.61, 91.59, 91.61 and 91.57 per cent., an average of 91.595 per cent. Our ratio between phosphorus and molybdic acid as computed on these analyses is 1.797.

We determined the molybdic acid in the filtrates from the phosphorus determinations and obtained 92.25 and 92.41 per cent. These results are higher than those previously obtained in the separate determinations, but as this difference was not sufficient to change to any extent our ratio we did not investigate the cause.

We now went a step further, in order to prove that the ratio between the phosphorus and molybdic acid in the yellow precipitate actually obtained in a steel analysis, is identically the same as that in the yellow precipitate shaken down from the prepared solution of phosphorus.

We separated a considerable amount of yellow precipitate from a steel containing 0.10 per cent. phosphorus, by Dr. Dudley's method of analysis, and after drying to a constant weight at 130° C. made the determinations of phosphorus and molybdic acid exactly as in the case of the previous precipitate, obtaining the following results: Phosphorus, 1.638 and 1.648 per cent., an average of 1.643 per cent. Molybdic acid, 91.63 and 91.67 per cent., an average of 91.65 per cent.

The ratio between phosphorus and molybdic acid given by these figures is 1.792, thus confirming our previous results and the generally accepted figure of 1.794.

From the work above outlined it would seem evident that the ratio of phosphorus to molybdic acid can be derived much more accurately from the analysis of the yellow precipitate than by the method suggested by Dr. Dudley.

The elaborate investigations of Hundeschagen (*Chem. News*, Oct. 4, 11, 18, 25, and Nov. 1, 1889,) have shown that ammonium phosphomolybdate is far more uniform when prepared under varying conditions than was formerly supposed. If the conditions of precipitation of the yellow precipitate are maintained constant, there is but little doubt as to its uniform composition. The ratio then becomes a question of the accuracy of the determinations of phosphorus and molybdic acid in the yellow precipitate. We have accordingly given the methods used for these determinations as completely as possible, in order to afford an opportunity for criticism and duplication.

Ratio between Iron and Molybdic Acid.—The ratio between phosphorus and molybdic acid being established, we then took up the ratio between iron and molybdic acid, as the investigations of Mr. Babbitt, *J. Anal. Appl. Chem.*, **7**, 165, and our own experience had indicated that the commonly accepted ratio, 90.76, is too high where the reductor is used, the reduction being considerably greater than with the ordinary method of reducing with zinc powder and shot.

Our first experiments were on the standardization of a permanganate solution by the ordinary method of dissolving the steel in a flask in an atmosphere of carbon dioxide gas, as compared with the figure obtained when the steel was dissolved in an open beaker and reduced through the reductor. No appreciable difference was found, the reduction being complete in both cases.

We then made a large solution of molybdic acid of such a strength that fifty cc. contained 0.25 gram of the salt. The first experiments with this solution were made after the reductor had been in use some time, and the zinc was packed closely together, so that the solution encountered considerable resistance to its progress, and the acid had some time to act on the zinc, the result being that the reductor became quite hot. Upon cleaning out the reductor and filling with entirely fresh zinc, we were surprised to find our results very appreciably lower, no matter how slowly the solution was passed through the reductor, and only after heating the solution nearly to boiling did we obtain the results in the first case. This demonstrates that care must be taken to have the solutions hot when they are reduced, in order to obtain complete reduction, but with this precaution the results are very uniform, as will be seen from the table following. In each of the following experiments fifty cc. of the above mentioned molybdic acid solution was used.

Experiments with reductor:

RESULTS EXPRESSED IN CUBIC CENTIMETERS OF PERMANGANATE.

	REDUCTOR CLOGGED FROM LONG USE.		REDUCTOR CONTAINING FRESH ZINC.		
	Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid, cubic centimeters.	Ten cc. sulphuric acid, cubic centimeters.	Five cc. sulphuric acid solution heated to 95° C., cubic centimeters.
	....	75.2	74.8	74.6	....
	75.25	75.3	75.0	74.7	75.45
	75.35	75.4	74.9	74.7	75.35
	75.45	75.3	74.95	74.8	75.35
Average,	75.35	75.3	74.91	74.70	75.38

Our experience with the reductor has been that in order to secure complete reduction, it is necessary to have the column of zinc of considerable length, and to pass the solution through

very slowly. We would not feel safe in using a column of zinc less than ten inches in length. In reducing a solution which has a bulk of 200 cc. at least two minutes should be allowed for passing through.

Turning now to the reduction of molybdic acid by heating with zinc and sulphuric acid, we found that very different results could be obtained by the various modifications of the method. These methods vary not only in the amounts of zinc and sulphuric acid recommended, but also in the temperature used and the time of heating.

We experimented with the method given in Chemical Analysis of Iron, by A. A. Blair, p. 97. Fifty cc. of our stock molybdate solution reduced in this manner required 73.23 cc. of permanganate.

We then reduced the molybdic acid solution as follows: Fifty cc. of stock molybdic acid were measured off, twenty grams of zinc (and four large shot) were added, together with thirty cc. of ammonia (1 : 3). This was heated almost to boiling, eighty cc. of hot sulphuric acid (1 : 4) added, and allowed to reduce for fifteen minutes, keeping the solution at a gentle boil. Fifty cc. of the stock solution reduced in this manner gave as a mean of a number of determinations 74.2 cc. of permanganate.

It will be noticed that there is quite a difference between these results, and also that the highest value obtained by the zinc and sulphuric acid method is considerably lower than that given by the reductor. In some laboratories the zinc and sulphuric acid method of reduction is used with a less amount of zinc, shorter time, and at temperatures which do not reach the boiling point. In such cases the reduction is certainly far from complete.

The mean of four gravimetric determinations upon this same solution show the amount of molybdic acid contained in fifty cc. to be 0.233264 gram. The average number of cubic centimeters of permanganate used in titrating this amount after being passed through the reductor is 75.35, hence one cc. permanganate = 0.003096 molybdic acid. A careful standardization of the permanganate solution against iron gave its value as one cc. = 0.003472 gram iron, hence the ratio between iron and molybdic

acid, when the reduction is made by means of the reductor in our hands gives 89.16 instead of 90.76 as found by Mr. Emmerton. This difference is readily accounted for by the difference in the method of reducing the solutions. Our figure tends to corroborate the work of Mr. Babbitt in this connection although it does not correspond exactly with the one he obtained. From the foregoing work it would seem that the ratio between phosphorus and molybdic acid of 1.794 is correct, but that where the reductor is used 89.16 represents more nearly the correct ratio between iron and molybdic acid, hence our results are computed on this basis.

The Effect of Temperature on the Precipitation of Arsenic.— With the exception of these factors we found no fault with the method given by Dr. Dudley and the uniformity of the results obtained was very gratifying. To divide the errors liable to occur in weighing out the sample, and for convenience in manipulation, we have altered the method slightly in the direction of using a larger sample of steel and smaller bulk of solutions. A large number of determinations have proved that we do not in any way decrease the accuracy of our results by these changes. In detail, the method, as used by us, is as follows: Dissolve 1.5 grams steel in seventy-five cc. nitric acid 1.135 sp. gr. in an eight-ounce Erlenmeyer flask, allow to dissolve on the hot plate and boil hard for about one minute after the steel is in complete solution. Add crystals of potassium permanganate until a permanent purple color is obtained which will remain for at least one-half a minute on boiling. In order to secure such a color, enough permanganate must be added to form a copious dark brown precipitate of manganese dioxide. The crystals of permanganate must be added carefully to prevent the solution from boiling over. Remove the flask from the plate and add ferrous sulphate free from phosphorus, with constant shaking, until the solution clears. Cool to 38° C. and add seventy-five cc. molybdic acid at 27° C. Shake hard for five minutes, filter off the yellow precipitate and wash with ammonium sulphate wash water until the filtrate shows no reaction for molybdic acid when tested as previously described. Dissolve the precipitate in ammonia (1:3), using as little as possible. Wash the paper once with water, and pass the liquid back through the filter and wash

thoroughly. The bulk of this filtrate should not exceed 150 cc. Acidify with five cc. concentrated sulphuric acid, and reduce with the aid of the reductor, passing the liquid slowly through a ten-inch column of zinc. Titrate with potassium permanganate.

Our next step was to ascertain if the method or any modification of it could be used in the presence of arsenic without serious error from that source. Solutions of arsenic were made up by dissolving arsenious oxide in a small amount of a solution of sodium acid carbonate, and diluting with nitric acid 1.135 sp. gr. The strength of these solutions was so adjusted that seventy-five cc. of each would correspond to 0.1, 0.5, and 1 per cent. of arsenic when 1.5 grams of steel are used. Blank experiments were first made with the chemicals to be used, following in every detail the method given. The average of the results obtained are given in the table which follows. We then shook down in the same manner the three arsenic solutions prepared as stated, trying the effect of different temperatures, but were unable to bring down any appreciable amount of arsenic as the table will show.

	Percentage of arsenic added.	Temperature of solution.	Temperature of molybdic acid.	Temperature of the mixture when shaken.	Result in terms of phosphorus, per cent.	Blank exper. on chemicals in terms of phosphorus, per cent.	Arsenic obtained in terms of phosphorus, per cent.
Blank exper.	..	85° C.	27° C.	52° C.	.....	0.0006	.....
Blank exper.	..	16°	16°	16°	.....	0.00034	.....
Blank exper. plus arsenic.	1	85°	27°	52°	0.0023	.....	0.0017
"	1	16°	16°	16°	0.0010	.....	0.0066
					0.00085	.....	0.0051
"	5	85°	27°	52°	0.0016	.....	0.0010
					0.0018	.....	0.0012
"	5	27°	27°	27°	0.0014	.....	0.0011
					0.0014	.....	0.0011
"	1	85°	27°	52°	0.0018	.....	0.0012
					0.0018	.....	0.0012
"	1	16°	16°	16°	0.0018	.....	0.0015
					0.0018	.....	0.0015

These tabulated results gave us no little surprise, being so entirely contrary to the behavior usually attributed to arsenic. But we have repeatedly duplicated them, confirming our first results in every case. To investigate the matter still further we made a solution of pure nitrate of iron and phosphoric acid of such a strength that twenty cc. contained approximately 1.5 grams of iron and one-half per cent. of phosphorus. Analysis of

this solution, made as before and shaken down at 85° C., gave 0.442 per cent. phosphorus, duplicate 0.446 per cent. On the addition of 0.25 per cent. of arsenic to this solution and shaking down at 85° we obtained 0.484 per cent. phosphorus, duplicate 0.489 per cent., or an increase of 0.4 per cent., due to the arsenic added. We then took the four samples of steel on which our previous work had been done, and to each of these was added 0.1 per cent. of arsenic and the analysis shaken down with the results shown in the following table:

	Arsenic added, per cent.	Temperature of solution.	Temperature of molybdic acid.	Temperature of mixture when shaken.	Phosphorus obtained before arsenic was added.	Phosphorus obtained after arsenic was added.	Arsenic obtained in terms of phosphorus.
Iron salt plus phosphoric acid.	0.25	85° C.	27° C.	52° C.	0.442	0.484	0.042
No. 27.	0.10	"	"	"	0.110	0.119	0.009
" 789.	0.10	"	"	"	0.021	0.022	0.001
" 344.	0.10	"	"	"	0.066	0.067	0.001
" 65.	0.10	"	"	"	0.012	0.012	0.000

As the arsenic in these determinations was precipitated under identically the same conditions as were previously used in our blank experiments, except phosphorus being present, it is reasonable to infer that the action is a mechanical one, the ammonium phosphomolybdate carrying down with it a little of the arsenomolybdate, the amount depending largely upon the size of the precipitate. Our results given above tend to demonstrate this quite conclusively. We repeated the above work using Wood's formula for molybdic acid, shaking for ten minutes instead of five, allowing the precipitate to stand for fifteen minutes before filtering off, to ascertain if any of these variations had any influence on the precipitation of arsenic. We found that they made no appreciable difference in our results. If the method is followed as outlined, and the temperature of the solutions is not higher than that specified, so that the actual temperature at which the shaking takes place does not exceed 49° to 55° C., the error will never be appreciable, except in the case of a steel very high in both phosphorus and arsenic. One point, however, we have been unable to check up, and that is if arsenic which has been reduced from the ore with the iron behaves the same as

arsenic artificially introduced. We were wholly unable to obtain a sample of steel containing an appreciable amount of arsenic, upon which to work, and have been obliged to leave this until some future time when we may be fortunate enough to secure the necessary sample.[1] It is conceded by every one that temperature is an all-important factor in the precipitation of phosphorus in the presence of arsenic. We know that above a certain temperature arsenic is sure to come down in greater or less amounts. The question then arises, how high a temperature is necessary for the complete precipitation of phosphorus, or in other words, how low a temperature can we use and feel sure we have precipitated all the phosphorus. Numerous experiments upon various samples of steel at 32° and 55° temperature have shown that the results at 32° C. are slightly lower. This difference does not usually exceed 0.001 per cent. if precautions are taken to thoroughly shake the solution, and to use a paper sufficiently close to hold every trace of the fine precipitate. In view of the fact that the difference between the results obtained at the two different temperatures is so slight, and also that there is danger of contamination in the case of a steel high in both phosphorus and arsenic, we adopted the lower temperature.

It may be asked how do the results obtained by this volumetric method compare with those given by gravimetric methods of wide reputation, such as the acetate method. We regret that we were unable to make acetate determinations of the phosphorus in the four standard samples of steel previously used, but our investigations of the molybdate method proved so much more exhaustive than we had anticipated, that these samples were used up in that work. However, we spent considerable time on a steel which had been examined by a number of well-known chemists. The results obtained by others are as follows:

Acetate method.	Molybdate method.
0.047 per cent. phosphorus.	0.059 per cent. phosphorus.
0.048 " " "	0.050 " " "
0.046 " " "	0.060 " " "
0.050 " " "	.....

[1] Since writing the above we have received, through the kindness of Mr. W. P. Barba, of the Midvale Steel Company, a sample of steel said to contain 0.093 per cent. phosphorus, and approximately 0.12 per cent. arsenic. The average of a number of determinations on this sample, by the above method, gave 0.095 per cent. phosphorus—thus confirming what we had previously observed.

Our results on this sample were 0.048 by the acetate method and 0.055 by the volumetric. By the combination method described above, which seems to exclude many of the chances of error which occur in either the acetate or molybdate method, we found 0.0538 per cent. phosphorus.

It will be noticed that the results obtained by the acetate method are lower than either of the others. This has been our experience repeatedly, when we have compared the three methods, the acetate giving invariably the lowest results.

We will not enter into a discussion in regard to the causes for this as they are many, and this is not the purpose of our paper, but in our opinion the proposed Committee on Standard Methods can do no greater benefit to the iron industry of our country than by a thorough investigation of the methods used for the determination of phosphorus in ores and finished products. From our personal observation we know that frequently injustice is done, and able chemists brought into disrepute, simply because their results have not agreed with those obtained by analytical chemists of wide reputation, whose methods have not told the whole truth.

ON THE QUALITATIVE DETERMINATION OF TANNING MATERIALS.[1]

By H. R. Procter, F. I. C., F. C. S., Lecturer on Leather Industries at the Yorkshire College, Leeds, England.

IT can hardly be said that any systematic attempt has been made to formulate a scheme for distinguishing the various tanning materials by their qualitative reactions, except perhaps a very slight table published by the writer, although, in view of the constantly increasing number of new tanning materials, and especially of new extracts which are offered to tanners, the matter has become one of considerable practical importance. The commercial value of an extract is dependent, not only on the percentage of tanning matter as determined by analysis, but on the nature of the tannin present, which influences the character of the leather produced.

It is, of course obvious, that, failing a clear knowledge of the

[1] Read before the World's Congress of Chemists, August 25, 1893. Proof of this article was kindly read by Professor Henry Trimble.

tannins themselves any definite scheme of separation is for the present impossible; since, although we have good reason to believe that the tannins are a class, we are quite ignorant of their number, which may easily be a comparatively small one, as many members of the group which at present receive individual names are probably mere mixtures. What can be done is to separate the tanning materials into groups or individuals by reactions which have been empirically determined; of which in many cases we do not know the chemical significance, and which may possibly be often due to other constituents of the materials than the tannins themselves. The question is still further complicated by the fact that woods, barks, and fruit of the same tree often yield tannins of distinctly different character. In view of these facts, the group tables given must be only regarded as pointing out the general character of the material examined, and their indications must always be confirmed by direct comparison of *all* the reactions observed with those given by the material suspected. It must also be remembered that in some cases the group reactions are uncertain, or may be simulated by mixtures, which may often be determined by comparison of the results of the more special tests.

In this connection it may be noted that most of the reactions under the intermediate groups might be simulated by suitable mixtures of A and F; and that the inconstancy of the iron reaction in closely allied trees, points either to their containing mixtures of tannins, or to the existence of a very large number of closely allied tannins of very similar constitution. The point is one very difficult of decision, since we have no really reliable method for separating different members of the family.

It was thought that some information as to the meaning of the reactions employed might be obtained by examining the behavior of the simpler derivatives under the same circumstances, and the results are given in table X. It will be at once obvious that the blue-black reaction with iron is characteristic of the pyrogallol group; and the green-black equally so of the catechol derivatives, while phloroglucol, contrary to the statements of the text-books, gives no marked reaction with iron, but is alone characterized by the very delicate reaction

with the vanillin present in deal. On the remaining reactions little light is thrown.

In qualitative work with tanning materials, a good deal depends on the strength of the solutions, and the way in which the tests are performed, and as the information in the Tables is necessarily very brief, a few preliminary words are desirable.

Infusions of tanning materials are understood to be of about the strength used by the writer in determinations by hide-powder, *viz.*, about 0.6 gram of dry soluble matter in 100 cc., but moderate divergencies from this do not influence results. Of course where reactions are feeble in any case, with very dilute solutions they may be imperceptible, and on the other hand, strong solutions will sometimes give precipitates where only colorations are noted with weak ones.

Bromine water reaction.—It is best to add the bromine water drop by drop to 2–3 cc. of the infusion in a test tube, until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline and on this account less conspicuous, but it is usually a distinct yellow or brown flocculent one. In most cases bromine precipitates such tannins as give a green-black with iron, and in general terms it may be said to be a reagent for the catechol tannins.

Nitrous acid reaction.—This reaction, which is believed to be a new one, is obtained by adding to a few cc. of the infusion in a porcelain basin a distinct excess of solution of sodium or potassium nitrite, and then 3–5 drops of decinormal sulphuric or hydrochloric acid. In typical cases the solution instantly turns pink or crimson, and slowly changes through purple to a deep indigo-blue, but in others, as sumach where the reaction is feeble, and masked by other changes, the final color is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown coloration or precipitate, but "reaction" in the Tables invariably means a series of color-changes as above described. Nothing can as yet be said on the nature of the chemical changes produced. The reaction is given by all tanning materials which yield ellagic acid or "bloom," but not by ellagic acid itself, nor by pure gallotannic acid. It is possibly a reaction of ellagitannic acid.

Ferric alum, Ammonio-ferric sulphate.—A one per cent. solution of this salt has been chosen as easily obtainable, neutral, and in a state of approximate purity. Ferric chloride, which is generally used, is almost invariably strongly acid, and of a very persistent yellow. Acid ferric chloride in excess will give a green-black reaction with gallotannic acid itself, and its results as a test are often very misleading. Ferric acetate, which has also been largely used gives heavy precipitates with most materials and is very strongly colored, so that it was found less convenient than the iron alum. As the colorations are generally very powerful, they are best seen by diluting the tannin infusion freely, and adding the iron solution very cautiously. In many cases the coloration first produced, and which is the characteristic one, rapidly fades to a dull olive or brown in presence of excess of iron, probably by oxidation and destruction of the tannin.

Cupric sulphate and ammonia.—When solution of cupric sulphate is added to a tanning material infusion, it sometimes gives a precipitate, and sometimes not. This is a useful indication in some cases, but must not be regarded as of first rate importance as the presence of any weak organic salt would in all cases cause a precipitate, by neutralizing the sulphuric acid of the sulphate. Cupric acetate produces a precipitate with all tannins so far as I have observed, and it is interesting to note that in this case, as in many others of a like character, the tannin combines with, and precipitates the salt as a whole. On the addition of ammonium carbonate, effervescence takes place, and the precipitate darkens, and becomes a true tannate.

When ammonia is added to the mixture of a tannin and cupric sulphate, a precipitate is invariably formed in the first instance, consisting of a tannate of copper with variable quantities of blue cupric hydroxide. With excess of ammonia, the whole of this precipitate is in many cases dissolved, while in others, an insoluble tannate remains. The latter is the case with all tannins derived from gallotannic acid and with many containing protocatechuic acid and forms a useful means of classification, though as yet the difference of structure to which it corresponds is unknown. The fact that hemlock and other

pine barks, as well as cutch and gambier, yield cupric tannates soluble in ammonia is an instructive commentary on processes which have been proposed for quantitative estimation by precipitations by ammonio-cupric solutions.

Where the precipitate redissolves it generally does so with the production of either a greenish brown, or a purplish brown coloration, which in presence of a small amount of the blue ammonio-cupric sulphate, appears either as a green or a reddish violet, and is again a useful means of identification. It need hardly be pointed out that to see this coloration well, the copper should be in the least possible excess. Hence it is desirable to use a very weak copper solution, say at most one per cent.

Stannous chloride and hydrochloric acid.—This reagent, the application of which is here first published, consists in a strong solution of stannous chloride in concentrated hydrochloric acid. If about ten cc. of this are added to one cc. of the tanning material infusion, in a porcelain basin, and allowed to stand for ten minutes, coniferous tans, mimosas, and some others give a very marked pink coloration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the coloration appears very strongly.

Deal shaving and Hydrochloric acid.—A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier, and a few other materials, the spot becomes at once a bright red or violet, but in many cases the reaction is faint, and only appears after some hours. It probably always indicates the presence of phloroglucol.

Sodium Sulphite—This was mentioned in my previous manuscript on the subject, but the printer unfortunately substituted sodium sulphide, which does not answer in the laboratory.

In some cases these reactions will serve to determine the constituents of mixtures but in many cases this will continue impossible till further and more distinctive reactions are discovered.

They can of course be applied to the recognition of tannates, when excess is present in leather which can be dissolved out

with water; but the effect of dilute alkalies and other solvents on the reactions is worth further experiment.

A few drops of the solution are placed in contact with a crystal of sulphite on a tile or in a basin. With valonia, a bright purplish pink is rapidly developed, apparently by oxidation. Many other tanning materials produce red or pink colorations, but in no case so marked a reaction as valonia.

Concentrated sulphuric acid.—A test tube is rinsed out with the infusion, and drained so that only about a drop remains, and concentrated acid is cautiously poured into the sloping tube, so as to form a layer underneath the tannin solution. The ring of color at the junction of the two liquids is noted, and then they are mixed by shaking, and diluted with water. About half the materials give a deep purplish crimson, called simply "crimson" in the Tables, and in many cases this is decidedly pink on dilution, while in other cases it is obscured by brown products formed by the heat of mixture. A large number of other materials give browns or yellows only, which when intense appear red, but dilute to yellows or yellow-browns.

Lime water is a most useful reagent, being very varied in the color of the precipitates it produces, and the changes they undergo by oxidation. The reaction is best seen in a shallow porcelain basin.

Qualitative Classification of Tanning Materials. Table I.

Bromine water produces a precipitate.				Bromine water produces no precipitate.			
Nitrous acid gives no reaction or merely darkens.		Nitrous acid causes a red coloration, becoming violet and blue or green.		Nitrous acid gives no reaction or merely darkens.		Nitrous acid produces a red coloration changing to violet and blue or green.	
Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.	Iron alum green-black.	Iron alum blue-black.
Copper sulphate followed by ammonia in excess.	Group B. Table V.	Group C. Table VI.	Group D. Table VII.	Group E.	Group F.	Group G.	Group H.
Precipitate is insoluble in excess of ammonia-Group A γ. Table IV.				No members of this group known but *catechol and protocatechuic acid*, which are not tannins.	Table VIII.	No members of this group known.	Table IX.
Precipitate redissolves with green or olive brown coloration-Group A β. Table III.				See Table X.			
Precipitate redissolves with reddish violet coloration-Group A α. Table II.							

TABLE II.

Group A *a*.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
Cutches from *Ac. catechu wood.*	Green-black.	pp.	No react. darkens.	pp. redissolves generally red-violet c'l'n.	No react.	Deep violet-red.	Reddens somewhat.	Red-brown coloration.	Reddish pp. slowly formed.
"Thaun leaf" extract (*a cutch substitute*).	Olive-black pp.	pp.	No react. darkens.	pp. redissolves brownish coloration.	No react.	No react.	No react.	Crimson, pink on dilution.	No pp.
"Turwar" bark. (*Cassia auriculata.*)	Green-black.	pp.	No react. darkens.	pp. redissolves red-violet.	No react.	Trace.	Pink coloration.	Crimson.	Reddish pp.
"Gambene" extract (a gambier substitute).	Green-black coloration.	pp.	No react. darkens.	pp. redissolves red-violet.	No react.	No react.	Slight pink coloration.	Crimson-pink diluted.	Reddish pp.
"Tengah" bark (*Ceriops Candolleana*).	Green-black coloration.	pp.	No react. darkens. pp.	pp. redissolves red-violet.	Pink coloration.	No react.	Pink coloration.	Crimson.	Bright red pp.
Bark (*Acacia leucophlœa*).	Green-black coloration.	pp.	No react.	pp. redissolves red-violet.	Pink coloration.	Slow violet react.	Pink coloration.	Crimson-pink diluted.	Dull brown pp.

TABLE III.

Group A. β.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ + NH_4OH.	$SnCl_2$ + HCl.	Deal Shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
Gambier, (ext. of leaves of *Nauclea gambir*).	Deep green coloration.	pp.	No react. darkens.	pp. redissolves olive-green.	Yellow.	Deep violet-red.!	Yellow.	Crimson dilutes brown.	No pp.
(1) "Purim Bast." (leaves of *Colpoon* or *Osyris compressa*).	Green-black.	pp.	No react.	No pp. pp. redissolves green.	No react.	Pink.	Yellow.	Crimson dilutes brown.	Light yellow pp.
(2) "Koko" natal, (leaves of *Celastrus buxifolia*.)	Green-black.	pp.	No react.	No pp. pp. redissolves green.	No react.	No react.	Yellow.	Dark brown.	Bright yellow pp.
Larch bark (*Larix Europæa*).	Green-black coloration.	pp.	No react. darkens.	pp. redissolves olive-green.	Pink coloration.	No react.	No react. darkens.	Deep red-brown.	Rusty pp.
Hemlock bark (*Tsuga* or *Abies Canadensis*.)	Olive-green reddish pp.	pp.	No react. pink with $NaNO_2$	pp. redissolves neutral tint.	Pink coloration.	No react.	Reddens.	Crimson dilutes pinkish.	Red-brown pp.
"Larch" extract (*Abies excelsa*). (3)	Green-black or brown.	pp.	No react.	pp. redissolves olive-green coloration.	Pink coloration.	No react.	Darkens.	Deep red-brown.	Brown pp.

(1) Used at Cape of Good Hope as sumach.

(2) Used in Natal as sumach substitute.

(3) *Fichte, Rothtanne* Norway or common spruce. *Abies pectinata* the *Weiss or Edel-Tanne* or silver fir is said to give a blue-black with iron.

TABLE IV.

Group A γ.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ + NH_4OH.	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
Willow bark. (Russian. Sp. unknown.)	Green-black.	pp.	No react.	Slight pp. — Dense pp.	No react.	Violet faint.	Pink coloration.	Red-brown not intense.	Slight greyish pp.
Acacia Angfica or Peptadenea macrocarpa.	Green-black.	pp.	No react.	Slight pp. — Dense choc'e pp.	Pink or violet color.	Violet faint.	Reddens somewhat.	Crimson dilutes pink.	Reddish pp.
Acacia catechu bark.	Green-black.	pp.	No react.	No pp. — Dense violet-black pp.	Possible trace.	Trace.	Pink color.	Red-brown.	Flesh color pp.
"Thorn tree" bark. (*Acacia horrida*) (Cape.)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Doubtful.	Pink color.	Dull crimson not intense.	No pp.
Mangrove bark extract. (*Rhizophora mangle.*)	Green-black.	pp.	No react.	No pp. — Reddish-black.	Slight reddening.	No react.	Slight reddening.	Red-brown.	Red pp. darkened by excess.
Quebracho wood extract. *Quebracho or* (*Loxopterygium Lorentzii.*)	Green-black coloration.	pp.	No react.	Slight pp. — Dense pp.	Pink color pp.	Trace.	Doubtful.	Crimson coloration dilutes pink.	Light brown pp.
"Sugar brush" bark. (Cape.) (*Protea mellifera.*)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Trace.	Doubtful.	Red.	Yellow-brown pp.
"Waagenboom" (Cape.) (*Protea grandiflora.*)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Trace.	Pink color.	Crimson dilutes pink.	Light yellow pp.
"Kruppelboom" (Cape.) (*Leucospermum conocarpum.*)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	Violet distinct.	Pink color.	Crimson dilutes pink.	Slight greyish pp.
"Silver tree" (Cape.) (*Leucodendron argentea.*)	Green-black.	pp.	No react. darkens.	No pp. — Dense pp.	No react.	No react.	Pink coloration.	Crimson dilutes pink.	Flesh color pp.

TABLE V.

Group B.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ + NH_4OH.	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
"Skens," Cypress Sumach (possibly *Coriaria myrtifolia*).	Blue-black pp.	pp.	No react.	Slight pp. — Dark pp.	No react.	No react.	Yellow.	Yellow-brown.	Yellow pp. dark'ning
Kliphant bark (1) (*Rhus Thunbergii*).	Blue-black.	pp.	No react.	No pp. — Dense dark pp.	No react.	No react.	Pink.	Dull crimson dilutes orange.	Pinkish pp.
Canaigre (Root of *Rumex hymenosepalus*).	Blue-black. pp.	pp.	No react.	Slight pp. — Dense dark pp.	No react. clouds.	Trace violet.	Slight dark'ning	Yellow-brown.	Pink coloration greyish pp.
"Talwaan" or "Elandsbortjes" (Root *Elephantorrhiza Burchellii*).	Blue-black pp.	pp.	No react. darkens.	Slight pp. — Dense dark pp.	No react.	Trace violet.	Pink.	Red.	Reddish brown pp.
Mimosa or Wattle bark (Various Austral. Acacias).	Dirty violet pp.	pp.	No react.	Slight or no pp. — Dense purple brown pp.	Slight reddening	Sometim's trace.	Reddens.	Crimson dilutes pink.	Reddish or yellow-brown pp.
Babool bark. India. (*Acacia Arabica*).	Dirty violet pp.	pp.	No react.	Slight or no pp. — Dense dark pp.	Some trace.	Faint trace.	Slight dark'ning	Crimson dilutes orange.	Dark reddish brown pp.
Dark red Austr. bark (Probably an acacia).	Dirty violet pp.	pp. needle crystals.	No react.	Slight pp. — Deep violet pp.	No react.	Faint trace.	Orange-pink.	Crimson dilutes pink.	Bright violet pp.
"White bark" *Algaroba blanca* South America (A *prosopis* or *acacia*).	Dirty violet pp.	pp.	No react.	No pp. — Reddish black pp.	No react.	Violet.	Reddens strongly.	Crimson dilutes pink.	Red pp. turning violet.

(1) Used at Cape of Good Hope.

TABLE VI.

Group C.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ and ammonia.	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.	
Cork bark (*Quercus suber*).	Green-black coloration	pp.	Reacts somewhat.	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.	
Green Oak (Ital.) (*Quercus Ilex.*).	Green-black coloration	pp.	Reacts faintly if at all.	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.	
Garouille, Root Bark of Kermes Oak (*Quercus Coccifera*).	Green-black coloration	pp.	Reacts	Slight pp. — Brown color.	No react.	No react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.	
Quercitron Bark (*Quercus Tinctoria*).	Green-black coloration	pp.	Reacts somewhat.	Slight pp. — Brown color.	No react. Light green.	No react.	Doubtful.	Crimson dilutes pink.	Reddish brown pp.	Dyes yellow with Al. and Sn. mordants.
Chestnut Oak (*Quercus Castanea*).	Olive-green coloration	pp.	Reacts distinctly.	Decided pp. — Insol. in excess.	No react.	No react.	Reddens.	Crimson dilutes pinkish.	Reddish brown pp.	Infusions fluoresce especially with ammonia.

TABLE VII.

Group D.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ and ammonia.	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.	
English Oak *Quercus Robur*.	Blue-black (green with excess).	pp.	Reacts somewhat.	Slight pp. — Dark brown pp.	No react.	Faint react.	Reddens.	Crimson dilutes pink.	Reddish brown pp.	
Jaft or Delicft. (1) Supposed oak product.	Blue-black pp.	pp.	Reacts red-blue.	Brown pp. — Dark brown pp.	No react. Dark brown pp.	Faint react.	Some dark'ning	Crimson dilutes pink.	Reddish brown pp.	Strong infusions, dry whitish and iridescent

(1) A Persian product, dark scales very rich in tannin (about forty per cent).

TABLE VIII.

Group F.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ + NH_4OH	$SnCl_2$ + HCl	Deal shaving and HCl	Na_2SO_3	H_2SO_4	Lime water.	
Aleppo galls (*of Quercus infectoria*).	Blue-black pp.	No pp. slight scum.	Reacts red to blue.	G'nish pp. — Dark pp. insoluble.	Light yellow pp.	No react.	No react.	Greenish to dirty yellow.	Pale pp. turning bluish-green.	
Sumach (leaf of *Rhus coriaria*).	Blue-black pp.	No pp.	Reacts feebly.	G'nish pp. — D'k brown insol. pp.	No react.	No react.	No react.	Yellow.	Yellow pp. turning bright green.	Dyes yellow on Sn mordants.
Myrobalans (*Terminalia chebula*).	Blue-black pp.	No pp.	Reacts red to blue.	Yellow pp. — Dark insoluble pp.	No react.	No react.	Yellow.	Yellow.	Yellow pp. turning greenish.	Dyes yellow on Sn mordants.
Pomegranate rind (*Punica granatum*).	Blue-black pp.	No pp.	Reacts red to blue.	Brown pp. — D'k brown insol. pp.	No react.	No react.	No react.	Orange-brown.	Bright yellow pp. turning red with exc'ss	
Algarobilla (pod of *Caesalpinia brevifolia*).	Blue-black pp.	No pp.	Reacts red to blue.	S'ht g'n pp — Dense dark pp.	No react.	No react.	Deep yellow.	Deep yellow-brown.	Bright yellow pp. darkens somewhat.	
Divi-divi (pod of *Caesalpinia coriaria*).	Blue-black pp.	No pp.	Reacts red to blue.	S'ht g'n pp — Dense dark pp.	No react.	No react.	No react.	Crimson.	Yellow pp. turning red-purple.	(1)
Algarobo (probably pod of *Prosopis dulcis*).	Blue-black pp.	No pp.	Reacts red to olive.	S'ht g'n pp — Dense dark pp.	No react.	No react.	Yellow.	Yellow to olive.	Yellow pp. turning black.	
Valonia (Cup of *Quercus Aegilops*).	Blue-black pp.	No pp.	Reacts red to blue.	No pp. — Dark red'ish pp.	No react.	No react.	Purplish pink.	Deep yellow.	Yellow pp. turning red-purple.	
"Oakwood" extract (oak or chestnut wood).	Blue-black pp.	No pp.	Reacts red to blue.	Pale pp. — Purple brown pp.	No react.	No react.	Reddens.	Yellow-brown.	Yellow pp. turning red-purple.	(2)

(1) Moderately strong potassium nitrite solution precipitates divi, but not *dilute* oakwood solutions; pp. soluble in hot, or *much* cold water.

(2) *Crude* chestnut wood extract may be distinguished from oakwood by its violet-reaction with ammonium sulphide (see "*Gerber*" No. 261, p. 157).

TABLE IX.

Group H.	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ and ammonia.	$SnCl_2$ + HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
Pure Gallotannic Acid.	Blue-black pp.	No pp.	No react.	No pp. — Dark pp.	No react.	No react.	No react.	Yellow.	Pale pp. turning blue.
Babool Pods. *Acacia Arabica.*	Blue-black.	No pp.	No react. darkens.	Slight pp. — Dark green color.	No react.	Faint violet.	No react.	Reddish violet.	Pink color. No pp.

TABLE X.

	Ferric alum.	Bromine water.	Nitrous acid.	$CuSO_4$ and ammonia.	$SnCl_2$ and HCl.	Deal shaving and HCl.	Na_2SO_3.	H_2SO_4.	Lime water.
Catechol.	Dark green coloration.	No pp.	Turns yellow.	No pp. — Green color.	No react.	No react.	No react.	Green coloration.	No pp.
Protocatechuic acid	Dark green coloration.	No pp.	Turns brown.	No pp. — No pp.	No react.	No react.	No react.	No react.	No pp.
Phloroglucol.	No react.	Bulky white pp.	Turns olive-green	No pp. — No pp.	No react.	Red-violet coloration.	No react.	Slight yellow.	No pp.
Pyrogallol.	Blue-black turning green and brown.	No pp.	Turns yellow.	No pp. — Brown color.	No react.	No react.	No react.	Brown coloration.	Violet colora'n rapidly turning brown.
Gallic acid.	Blue-black coloration.	No pp.	Turns brown.	No pp. — Brown color.	No react.	No react.	No react.	No react.	White pp. rapidly turning blue.

THE IMPORTANCE OF THE STUDY OF BIOCHEMISTRY.[1]

By E. A. de Schweinitz, Washington, D. C.

WHEN the controversy between the two schools of the vitalists and chemists as to the true cause of the diseases produced in animals by the inoculation of putrefactive organic matter was at its height, Panum, of Denmark, made some careful researches and extracted from putrid organic matter chemical substances, which, when perfectly free from every form of germ life, produced intoxication and death. But, he said the poison extracted from this putrid matter is undoubtedly a pure chemical compound, it may, however, be produced by a microbe, and both microbe and poison play their part in the disease.

Now more than fifty years later, though the microbian origin of most diseases has been thoroughly established, it has also been shown that the chemical products of these germs are the direct cause, in most instances, of the fatal effects. For example, in diphtheria the growth of the germ is but a local manifestation, while the poison it produces is distributed through the whole system. When, however, the germ has been discovered that is responsible for a disease or for other changes, to which we will presently refer, the door has but been opened for a study of the most interesting chemical problems that can be imagined. Germs in general are cells of protoplasm, and it is by a study of their actions and the changes which they produce that we can gain a better insight into the processes of life. Fortunately the majority of germs can be easily cultivated artificially, so that it is not difficult to obtain solutions of their products, but it is difficult to isolate these products from the solution and determine their nature. For the most part the substances produced by bacterial growth have been found to belong to two classes, the albuminoids and ptomaines, the latter corresponding closely in many of their properties and composition to the vegetable alkaloids. Our knowledge of the albuminoids, however, is very meager. We can divide them into certain general classes as 1, globulins; 2, albumoses (hemi-proteo or deutero albumoses),; 3, alkali or acid albumen; 4, peptones, etc.; but with this we have only made a step in the dark as it has given no idea of the actual

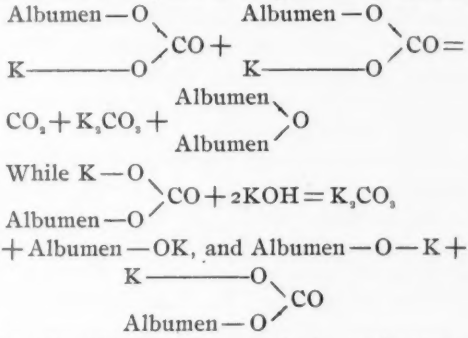
[1] Read at the Baltimore meeting, December 28, 1893.

composition of the substances about which we speak, beyond that they contain carbon, hydrogen, oxygen, nitrogen, and sulphur, and phosphorus in certain proportions, and differ in coagulation. Do these apparent albuminoid substances from bacteria belong to the class of albumoses, or are they chemical disastases or ferments, many of the reactions of which they show? Can they be proved to be diastases by their hydrating and digesting action and shown to be allied to ptyalin, pepsin, etc.? At first it was held, and is still held by some, that the presence of albuminoid matter was necessary to the growth of the germ and that the products of the germ life were changes or simply decomposition products of the albuminoid matter upon which they fed. But it has been proven too that some of the same substances are obtained by the simple action of acids and alkalies upon albuminoids, and it is often difficult to decide whether the albumoses and alkaloids have been produced by the germs or by the alkali or acid. To decide this it is necessary to cultivate the germs upon solutions which do not contain a trace of albuminoid matter. This Fermi and Uschinsky have succeeded in doing with a number of different germs upon a solution of glycerine and mineral salts (ammonium phosphate, and acid potassium phosphate), and I have also with the hog cholera, glanders, and recently tubercle bacillus by the addition of asparagine to the above liquid. From these cultures albuminoid substances have been obtained as well as alkaloids, showing that they have truly been built up and elaborated by the germ and are to be compared to intercellular secretions and excretions of these minute forms of life, and not to simple products of decomposition from albuminoid matter in solution. That the products formed under the different conditions are similar is shown by the same physiological action of mallein prepared from these artificial cultures or from cultures upon beef broth. This power of the germ to multiply upon a solution of mineral salts where the carbon, hydrogen, nitrogen, and phosphorus are present in an easily assimilable form is not surprising, for we deal here with the lowest form of vegetable life, and it is well known that plants cannot live upon albuminoid matter directly, but only when by decomposition it has been reduced to its elementary condition.

The study of these products of the germ life has made but little progress so far as their actual chemical constitution is concerned. Much more attention has been paid to their physiological effect. It has been learned that some of these products will render an animal insusceptible to the action of disease germs, but what the chemical change which can have taken place and caused this immunity may be, is one of the problems for the biochemist and physiologist to decide.

It has been found too that the blood serum of animals that have been made immune to disease has a germicidal action and will render other animals immune. Where does this property lie? What chemical change again has the blood undergone?

In his studies upon the albuminoids of the egg, Scholl has indicated where this property may be. He found that egg albumen exerted a germicidal effect, that this germicidal power was destroyed by heat and could be restored by treating the albumen with alkali. This was similar to some of Buchner's observations upon blood serum, where he found the bactericidal property could be restored by the use of an alkali. Scholl's theory for explaining this, and also at the same time the coagulation of albumen, is that the normal albumen has a composition corresponding to a bicarbonate, that upon heating, carbon dioxide is given off and the albumen coagulated by the consolidation of two molecules, while when the alkali albumen is heated no decomposition will take place or coagulation of the albumen.



$$\text{While } \text{K}-\text{O}\diagdown\!\!\diagup\text{CO} + 2\text{KOH} = \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{Albumen}-\text{OK}, \text{ and } \text{Albumen}-\text{O}-\text{K} + \text{CO}_2 =$$

The carbon dioxide in the albumen is also set free by acid in the

cold which will explain the coagulation of albumen by acid. In the albumen molecule then, there is a group of atoms with a bactericidal action, which grouping is destroyed by heat and restored by alkali, just as there are certain groupings necessary for the production of a disinfectant, or rather just as the disinfectants are characterized by certain groups. The confirmation of these experiments will open up a field of enormous possibilities, as sulphur is an element which in many cases can replace oxygen, and the resulting compounds would be very interesting, as well as lead to a number of new products and eventually to a better understanding of the albuminoid molecule.

As just mentioned, it has been found that in the case of a great many diseases, animals can be made insusceptible by vaccination, and that the blood of such immune animals will make others immune. But this immunity only holds for the particular disease against which the animal was first vaccinated, and does not protect the animal against another disease. A guinea pig can be protected from a hog cholera inoculation by an injection of the albuminoid product extracted from the cultures. The same pig will die if inoculated with swine plague. If, however, it be vaccinated both for hog cholera and swine plague, with the products extracted from their respective cultures, the animal will be insusceptible to both diseases. Just in the same way in each particular disease some chemical change is produced in the blood or tissues and the work of the chemist should be to find out what these changes are. The possibilities are enormous, the difficulties many, but by careful study, accompanied necessarily with a certain amount of bacteriological work and the observation of pathological changes, we can hope to arrive at a more definite understanding of the process of life.

It is, however, not only with reference to diseases that a study of biochemistry is important. From a practical and commercial standpoint the work is useful. J. A. Davalos, of Havana,[1] describes the isolation of a distinct ferment and a number of bacilli from different tobacco leaves, some of which in artificial culture give distinct poisons. The different varieties of tobacco show different germs. These germs, by their growth upon the

[1] *Cronico Medico-guirurgica de la Habana, 1892.* No. 15.

tobacco, give to it its peculiar flavor and odor, and the different qualities of tobacco owe their value to some particular ferment. As I have noticed, a bright yellow American high grade tobacco shows the presence of a germ altogether different, producing different substances from that of a low grade tobacco. Therefore, if the germs of a low grade tobacco can be destroyed and those from a fine tobacco substituted, we should be able to greatly improve the manufactured article. Now in practice, before the fermentation, some good tobacco is often mixed with the poorer grades to improve the quality. The manufacturer has learned by experience to make use of the different germs of the tobacco. But the chemist should not stop here. He should find out what the products of the growth of these germs are. This is possible because the germs can be isolated, cultivated, and the product of each individual germ determined, and eventually its identification or synthetic preparation.

Again, in Denmark, the practical manufacture of butter and cheese has been greatly advanced by the use of butter ferments, as they have been called. The flavor and aroma of butter and cheese are due to the products of a particular bacterium, or of several. Now these can and have been isolated, and to produce the best butter and cheese only those bacteria are used upon sterilized milk which give a desirable flavor, while normally those with undesirable products would also be present and interfere with the character of the butter and cheese. Here again the products of the growth of these bacteria should be studied, which in many instances would no doubt be found to be substances of easy synthetic preparation. It would be very much better to be able to add to a butter or cheese some particular extract which will impart the special flavor, rather than to have to inoculate the cheese and milk with a particular bacterium or mixture of bacteria for a desired quality. As has been well stated, we may see the time when each dairy is provided with a bacteria farm, and each particular brand of butter and cheese will have its corresponding originator, labeled and reared with as much care as is given to the cow from which the milk is obtained.

In their relation to the soil and plant life the germs and their

products are invaluable. Warrington and Winogradsky, in their isolation of the nitrifying organisms which convert nitrogenous matter into nitrites and nitrates, have thrown great light on the absorption of nitrogen by plants. Recently Winogradsky has described an organism which converts the nitrogen of the air directly into nitrates. Again, there are a number of germs that are ordinarily found in water or the soil which will reduce nitrates to nitrites or ammonia, as well as some pathogenic germs usually present in the soil which will flourish in artificial media in an atmosphere of nitrogen. We know that a subsoil, freshly turned, will not be productive until it has been exposed for some length of time to the air and moisture and to the action of the germs of the air. The plant does not take up directly in the form in which it exists in the soils, the mineral matter that it needs for its growth, but only when that is modified to a simpler form can it be utilized. Phosphorus is one of the elements which, whether combined in albuminoids or mineral salts, seems to be necessary for the growth of the germ, and is also necessary for the life of plants. By closely following the gradual changes in the artificial cultures of germs, we can arrive at a more definite understanding of the assimilation of mineral matter by the plant, as well as the fixation of carbon, the formation of starch and sugar, and possibly also, as has been suggested, of the building up of alkaloids.

I have only mentioned a few of the many directions in which a conjoint study of bacteria and their products are important with the desire of emphasizing the interest attaching to such investigations. It is along this line of research that the solution of many of the problems of life that have been a puzzle to both physiologist and chemist undoubtedly lies.

DETERMINATION OF THE CRYSTALLIZABLE SUGAR IN THE BEET.[1]

By H. Pellet.

Translated and Abstracted by G. L. Spencer, Washington, D. C.

THIS is an extensive article including a résumé of practically all that has been written by the leading authorities upon

[1] Read before the World's Congress of Chemists, August 22, 1893.

the subject, in addition to original methods by the author. The paper is divided into five parts.

The first part contains a brief outline of the methods employed for the determination of sugar since the beginning of the industry, or in fact since the work of Margraff on the beet in 1747, and includes the literature of 1886.

In the second part is included a review of the principal prizes which have been awarded for researches on the estimation of sugar in the beet.

In the third part is given a résumé of the different methods which may be applied for the direct determination of the sugar, and the principal details of the new cold and warm aqueous methods, as applied in the manufacture of sugar and the analysis of mother beets.

In the fourth part is given an examination of the matters existing in the beet which influence the determination of the sugar, notably raffinose, pectic substances and asparagine.

Finally, in the fifth part, note is made of the purchase and sale of beets according to their quality, and an examination of the various methods employed for this purpose is included.

This abstract relates simply to that portion of the third part of the paper which includes methods original with the author.

PROCESSES WHICH MAY BE APPLIED TO THE ANALYSIS OF THE BEET FOR THE DIRECT DETERMINATION OF THE CRYSTALLIZABLE SUGAR WHICH IT CONTAINS.

The different methods may be divided into two classes, namely, chemical and physical (polariscopic). As the polariscopic methods are those usually employed we will omit a description of the chemical. The polariscopic methods may be divided into two groups; those employing alcohol as a solvent for extracting the sugar and those employing water. The process employing water, with which we shall specially deal, is that devised by the author and known as the method of instantaneous aqueous diffusion in the cold. In the instantaneous method, it is essential to obtain the beet pulp in an extremely fine state of division. Ordinary rasps cannot be employed for this purpose. For the analysis by this method the following rasps are recommended: First, for the analysis of entire beets, the conical rasps of Pellet

and Lomont as arranged by Keil; second, for the analysis of fragments of beets such as fresh cuttings for the diffusion process, the apparatus of R. Kiehle, of Leipzig; third, for the analysis of seed beets, or mother beets, in seed selection, the apparatus of Keil and Dolle, known as the *foret-râpe*. The rasp used in connection with the apparatus of Hanriot is applicable.

As has been stated, for this process the pulp must be in a very fine state of division, not merely forming a cream, but the particles must be regularly even. A suitable amount of the pulp, proper precautions being taken to protect it, is weighed into a flask of a definite volume. If the normal weight for the German instruments, 26.048 grams, is used the volume should be 201.35 cc., or if 25.87 grams of pulp be taken the volume should be 200 cc. The pulp is passed into the special flask with the assistance of a jet of water, then five to seven cc. of subacetate of lead (30° B.) are added and a little ether to reduce the foam, the flask being agitated with a rapid circular motion at the same time. The volume is now completed to 200 or 201.35 cc. as the case may be, and the contents of the flask thoroughly mixed. Filter and polarize after having acidulated the liquid with one or two drops of glacial acetic acid. A 400 mm. tube is used for the observation and gives the reading directly, corrected for the increase in volume of the solution. The diffusion is instantaneous and complete, permitting the filtration to be made as soon as the flask has been filled to the graduation and the contents thoroughly mixed. It is never necessary to heat the solution in order to insure complete diffusion, unless the water should be extremely cold, approximating 0° C. For all ordinary laboratory temperatures, the water will be sufficiently warm.

In order to make a large number of analyses per day, by this process, a filtration rack having six, twelve, or twenty-four holes, should be employed, also a continuous polariscope tube which will be described later on. Twelve to twenty flasks should be taken at once to the polariscope.

Among the different possible sources of error in the estimation of the sugar in the beet, those belonging only to the aqueous method will be here considered. In the aqueous process there is, of course, a possibility of the digestion or diffusion being incom-

plete, but this is very rare, since, owing to the simplicity of the operation, the flasks will always stand a sufficient time to obtain complete diffusion. In using the apparatus in the cold there is no danger at all of error, since a preliminary trial should be made to ascertain whether the pulp is sufficiently fine, and whether the water is of the proper temperature. There is a possibility of the solution of pectic substances which rotate the plane of polarization to the right. This error can only result from an insufficient amount of sub-acetate of lead. This inconvenience is easily avoided. The presence of pectic bodies may be shown in the following manner: Extract the pulp with cold water in large excess or with alcohol; treat the residue with boiling water and concentrate the liquid. This liquid will give a decided right-handed polarization amounting to more than 6.87 per cent. sugar on the weight of the beet. The same liquid, treated by sub-acetate of lead in sufficient quantity, will always polarize zero. Our work in this case is confirmed by Messrs. Chevron, Droixhe, and Weisberg.

Alcohol acts as sub-acetate of lead upon pectic matters and precipitates them entirely. It is for this reason that in the alcoholic solution two or three drops of sub-acetate of lead are sufficient for clarification, and for the complete precipitation of the pectic matters. It is hence easy to see how different results may be obtained in using the alcoholic or the water method upon the same pulp. Such differences might amount to from two to three per cent. of sugar calculated on the weight of the beet. As we have become better acquainted with the sources of error, the experiments have been repeated, and the adversaries of the aqueous method have all recognized that there are no plus polarizing substances in the beet not precipitable by lead and which are only thrown down completely, as they have stated, by alcohol.

In 1886 and 1887 many chemists published articles in which they attempted to demonstrate that alcohol, in fact, furnished results lower than those obtained by the water method, and which they then attributed to some particular substances precipitable by alcohol, and not by the sub-acetate of lead. But all have acknowledged later on that there were evidently diverse causes of error in their experiments, and have published statements

reviewing those made in their first papers, and have shown perfect concordance between the alcoholic and aqueous methods, when properly carried out. This is quite valuable, since at first the aqueous methods were vigorously attacked by critics who now acknowledge their reliability. There is still another possible source of error in the aqueous method in the cold. This is caused by air bubbles remaining attached to the pulp, and may be due to an insufficient use of ether, to ether being replaced by alcohol, to insufficient agitation, or to other faulty manipulations. This error, it may be seen, is easily obviated. Numerous parallel experiments have demonstrated that the aqueous instantaneous method in the cold, gives practically the same results as those obtained by either the alcoholic or the hot water methods.

APPLICATION OF THE INSTANTANEOUS AQUEOUS DIFFUSION PROCESS IN THE COLD TO THE EXAMINATION OF MOTHER BEETS.

A portion of the pulp may be removed from the beet by the *foret-râpe* of Keil and Dolle and analyzed as described. This requires simply a weighing and the usual manipulation. A simpler method, and one which will be described more in detail, obviates all weighings. In this method of working, that is without weighing, 8,300 analyses per day have been made in the establishment of Mr. Legras, and in the sugar house of Vaux sous Laon.

In the analysis of beet mothers without the use of a balance, the sound invented by Lindeboom is employed. This sound is so arranged that by the movement of a lever, a knife is made to penetrate the beet and remove a portion of it. A proper arrangement is provided for inclining the beet at a proper angle to the knife. The knife is arranged with parallel blades which are adjustable, and which will remove a cylindrical portion of the beet of a size which is perfectly under the control of the operator. After adjusting the knife to cut a cylinder of a certain size, which is determined by the convenience of the operator, it may be used for a number of samples and will cut a cylinder of practically the same weight at all times. The weights of the following cylinders cut in this way will give an idea of the accuracy of this method:

No.	Weight, grams.
1	6.245
2	6.265
3	6.290
4	6.370
5	6.245
6	6.285
7	6.365
8	6.250
9	6.335
10	6.240
11	6.330
12	6.390
13	6.370
14	6.270
15	6.310
16	6.300

Average, 6.304 grams.

If one will consider a beet of average richness as containing fifteen per cent. sucrose the minimum weight given in the above list would show 14.85 sugar and the maximum 15.2, an extreme difference of 0.35 or 0.15 to 0.20 above and below the mean. These figures approximate the required weight with sufficient accuracy for actual practice and for use with the special apparatus devised by Hanriot, we have found it a very valuable adjunct. Hanriot's apparatus is so arranged that the sample of beet, of the required weight, when placed in a proper receptacle is transferred to a mill where it is ground to a fine pulp. Immediately after grinding, by a suitable manipulation of a valve and rubber bulb containing water, the fine pulp is washed into the sugar flask and is ready for analysis. The Hanriot apparatus is then quickly washed, by means of a special valve arrangement, and is ready for another sample. Preliminary to commencing the analytical work, the sound is adjusted to give the most convenient weight of pulp, for the polariscope in use. This may be 6 grams, 5.12 grams, or 4.05 grams, according to the requirements of the instrument. But little adjustment is necessary to so set the knives that they will cut a cylinder of the proper diameter and length to give the required weight. In this class of analysis, it is unnecessary to take account of the influence of the volume of the marc of the beet.

In the analysis of seed beets, Mr. Hanriot has suggested the use of electric signals for assorting the roots. Electric contacts are arranged on the scale of the instrument so that when this is turned to a certain point, corresponding to a certain richness of the beet, a signal will be sounded on a bell, and when turned to a certain other point a signal will be sounded on a bell of different tone, indicating in general the richness of the sample and showing the workmen how to distribute the roots.

CONTINUOUS TUBE FOR THE POLARIZATION OF ALL SOLUTIONS.

In many cases the manufacturer of sugar, the refiner or the seed producer, is obliged to make a very large number of analyses of the same class and as rapidly as possible. The work required in seed selection is an example. In this industry it is often necessary to make 3,000, 4,000, 5,000, and even 8,000 or more analyses of mother beets in a day.

With ordinary apparatus it is admitted that with one polariscope a single observer may make from 500 to 600 or even 1,000 analyses in a day, provided one has a sufficient number of observation tubes, that is, from twenty to fifty. The continuous tube permits this work with much less labor, far greater rapidity and requires but one observation tube. This instrument was devised especially for use in the analysis of mother beets.

Many difficulties were overcome before this tube was constructed in a satisfactory form. As now used there is a small tube at each extremity, one of which is termed the funnel and connects directly and exactly at the extremity of the observation tube against the glass; the other is a similar tube but is placed at a slight angle with the observation tube. This small tube connects with the sink and is used to get rid of the solutions after they have been polarized. This arrangement of the observation tube permits the displacement of one solution by another. In practice, the observation tube is never removed from the polariscope. At the start it is filled with water, slightly acidulated with acetic acid, care being taken to remove all air bubbles. The solution to be observed is now passed in at the funnel tube displacing the water, driving it out through the tube at the opposite end. When another solution is ready for examination, it is

simply necessary to pour it into the funnel and, as before, displace the preceding solution. The chemist at the polariscope will at first observe striae, which diminish rapidly, and finally the solution will become perfectly clear. As soon as the liquid becomes clear the observation may be made. While the chemist is entering the reading in his note book, an assistant introduces a new solution at the funnel, and the instrument is ready for another observation. In this way an observer can easily make four readings in a minute, but even if he could make but two, he would attain a speed twice as great as is possible with the ordinary polariscopic methods and with far less labor. In the analysis of beet mothers, where a slight difference is of no importance, an observer can easily make from six to ten readings per minute.

A special disposition of the apparatus may be made which permits filling the tube by siphonage. In this way from eight to twelve solutions per minute may be polarized.

EXPERT TESTIMONY.

By Wm. P. Mason.

A NUMBER of years ago several very able articles appeared in *Nature*, upon the subject of Expert Testimony, showing how desirable it is to have the scientific witness removed as far as possible from the position of a partisan, and suggesting that such an end could be best obtained by having the experts employed by the bench rather than by the bar. Some recent experiences of my own, which I beg permission to recount, call to my mind those "Nature" articles very forcibly. A poison case in which I was lately employed, may be roughly outlined as follows:

Much arsenic and a very little zinc were found in the stomach.

The body had not been embalmed, but cloths wrung out in an embalming fluid containing zinc and arsenic had been spread upon the face and chest.

Medical testimony showed that no fluid could have run down

[1] Read at the Baltimore meeting, December 28, 1893.

the throat. Knowing the relative proportions of zinc and arsenic in the embalming fluid, the quantity of arsenic found in the stomach was twelve times larger than it should have been to have balanced the zinc also there present, assuming them to have both come from the introduction of the said embalming fluid by cadaveric imbibition. Other circumstantial evidence was greatly against the prisoner.

At the time of my appearing for the people, on the occasion of the first trial of the case, my direct testimony brought out very strongly the fact of a fatal quantity of arsenic having been found in the stomach, but no opportunity was given me to testify to the presence of the zinc found there as well, although the fact of its existence in the body was known to the prosecution through my preliminary report. Through ignorance of the nature of such report on the part of the defence, no change was made in the character of my testimony during the cross-examination, and I was permitted to leave the witness-stand with a portion of my story untold. No witnesses were called for the defence, and the case was given to the jury with the darkest of prospects for the prisoner.

For many reasons, unnecessary to recount here, I was distinctly of the opinion that murder had been committed, but I felt nevertheless that common justice demanded that the prisoner should have been entitled to whatever doubt could have been thrown upon the minds of the jury, no matter how far-fetched the foundations for such doubt might have been.

The first trial having resulted in a disagreement of the jury I was pleased to learn, before the second hearing of the case began, that the defence was prepared to go into the question of the embalming fluid, for the responsibility of permitting only a part of what I knew to be drawn from me, to the entire exclusion of the remaining portion, was greater than I wished to assume. The nature of my report to the coroner having been established, and certain opinions relating thereto having been fully ventilated, the jury were possessed of "reasonable doubt" and acquitted the prisoner. What now were the duties of the expert upon the occasion of the first trial of this case and how should he have constructed the meaning of his oath.

One eminent legal light, to whom the question was referred, held that the expert was distinctly the property of the side employing him, and that his duty was simply to answer truthfully the questions put to him, without attempting to enlighten the court upon facts known to him, but not brought out by the examination, no matter how vital such facts might be.

Another held that although the above course would be proper in a civil case, yet in a matter involving life and death the witness should insist upon the court becoming acquainted with his whole story. Do not such differences in legal opinion make it yet more desirable that the expert, at least in capital cases, should be the employee of the bench, rather than of the bar, in order that whatever investigations are made may be entirely open to public knowledge and criticism?

DISCUSSION.—Dr. Wiley: I hope that at some time in the future we shall be able to discuss this subject more fully. It is one which vitally interests most of us.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—NO. 2.]

A NEW METHOD OF ANALYZING FATS AND RESINS.

BY PARKER C. MCILHINEY, PH.B., A. M.

Received January 5, 1894.

A number of processes have been proposed and used for the analysis of fats depending upon the power possessed by their unsaturated constituents to absorb by direct addition two or four atoms of bromine or iodine.

Allen, *Analyst*, **6**, 177, proposed the use of an aqueous solution of sodium hypobromite to be added to a weighed quantity of the oil together with sufficient hydrochloric acid to liberate the bromine which then acts upon the oil. An excess having been added its amount is determined with sodium thiosulphate after adding potassium iodide.

Mills and Snodgrass, *J. Soc. Chem. Ind.*, **2**, 436, added a solution of bromine in carbon disulphide to a solution of the fat in the same solvent until an excess has been added as indicated by the red color of the bromine remaining permanent for fifteen

minutes, and then a solution of potassium iodide and determined the excess with thiosulphate.

Mills and Akitt, *J. Soc. Chem. Ind.*, **3,** 65, proposed to substitute carbon tetrachloride for carbon disulphide and to determine the excess by a solution of β naphthol in the same solvent.

Hübl, *Dingler's Poly. J.*, **253,** 281, and *J. Soc. Chem. Ind.*, **3,** 641, suggested the use of a solution containing twenty-five grams of iodine and thirty grams of mercuric chloride dissolved in one liter of alcohol, a known measure of the reagent to be added to a weighed portion of the oil and allowed to remain tightly stoppered for a certain length of time when the excess is determined with thiosulphate.

Levallois, *J. pharm. chim.*, *1887*, **1,** 334, used bromine water, adding it, in just sufficient excess to slightly color the liquid, to the fatty acids obtained from the oil suspended in water.

Halphen, *J. pharm. chim.*, *1889*, **20,** 247, used bromine water in excess determining the amount of excess with sodium hydroxide.

Gantter, *Ztschr. anal. chem.*, *1893*, 178, suggested the use as a reagent of iodine dissolved in carbon tetrachloride.

The aim of all these processes is to determine the amount of halogen which the substance under examination will absorb by addition, but the figures obtained represent this only approximately even when substances which easily form substitution products are absent. Some substitution takes place with almost all oils, and with rosin oil, rosin, and probably most other resins, substitution causes the entire absorption.

The extent to which this substitution takes place depends upon the nature of the substance operated upon ,and varies with different oils and resins, and a determination of the amount of halogen so absorbed may serve as a means of identifying and in some cases determining them.

The following process has been devised for determining the amount of bromine which oils and resins can absorb by addition, (which will be called the "Bromine Addition Figure"), and at the same time the amount of bromine which replaces hydrogen the action being allowed to continue eighteen hours in the dark; this gives the "Bromine Substitution Figure." The first figure

gives in most cases the same information as the Hübl figure but is more reliable, while the second figure is a measure of the activity of the saturated constituents toward bromine.

It depends upon the fact that bromine in forming substitution compounds forms a molecule of hydrobromic acid for every atom of bromine which replaces hydrogen, while in forming additive compounds no hydrobromic acid is formed.

It was found impossible to use iodine alone as the addition figures are then very much too low and there is little difference between the substitution figures of bodies of unlike character.

The following solutions are used:

Bromine in carbon tetrachloride..... $\frac{N}{3}$
Sodium thiosulphate..... $\frac{N}{10}$
Potassium hydroxide..... $\frac{N}{10}$

0.250–1.000 gram of the substance is dissolved in ten cc. of carbon tetrachloride in a bottle of 500 cc. capacity provided with a carefully ground glass stopper. An excess of bromine solution is added, the bottle tightly stoppered and placed in a dark closet. No water or alcohol should be present and light should be excluded as far as practicable. At the end of eighteen hours the bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing about one and one-half inches long is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted when the water will be sucked into the bottle and dissolve the hydrobromic acid present. When about twenty-five cc. of water have been added in this way, the bottle is well shaken and 10–20 cc. of twenty per cent. potassium iodide solution added. The excess of bromine acts on the potassium iodide, liberating a corresponding amount of iodine which is titrated with $\frac{N}{10}$ thiosulphate after adding about seventy-five cc. more water, using starch as an indicator. The total bromine absorption is calculated from the difference between the amount of thiosulphate required for the bromine solution added and the amount required for the excess. The contents of the bottle are now transferred to a separatory funnel and the aqueous portion separated, filtered through a cloth filter, a few drops of thiosulphate added if the solution is blue, and this is then titrated with $\frac{N}{10}$ potassium

hydroxide using methyl orange as indicator. The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with $\frac{N}{10}$ hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimeters of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine substitution figure because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine substitution figure subtracted from the total absorption gives the bromine addition figure.

The following results were obtained:

Substance.	Total bromine absorption, eighteen hours.	Bromine, addition figure.	Bromine, substitution figure.
W. G. Rosin	212.7	0.0	106.35
E. Rosin	206.5	0.0	103.25
Second run Rosin Oil (a)	116.2	0.0	58.1
" " " " (b)	114.7	0.0	57.35
American Raw Linseed Oil	102.88	102.88	0.0
Same Oil Boiled	103.92	103.92	0.0
White Salad Cotton-seed Oil	65.54	64.26	0.64
Sperm Oil	56.60	54.52	1.04

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use. Rosin oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined. Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

ON THE DETERMINATION OF PHOSPHORIC ACID.[1]

BY H. PEMBERTON, JR.

LAST autumn I described a process for determining phosphoric acid by titration of the ammonium phosphomolybdate with standard alkali. (This JOURNAL, **15**, 382.) The ratio

[1] Read at the stated meeting of the Chemical Section of the Franklin Institute, held February 20, 1894.

between the P_2O_5 of the precipitate and the standard alkali was determined and found to be 23.2 molecules of Na_2O to one molecule of P_2O_5. Upon this ratio, as determined by direct analysis, the standard solution was prepared of such strength that one cubic centimeter should be equal to one milligram of P_2O_5 by diluting 326.5 cubic centimeters of normal alkali to one liter. The analyses upon which this ratio (23.2 molecules) was determined were carefully made. I was, therefore, at a loss to know the cause of the variation of this figure from the theoretical ratio of exactly twenty-three molecules of Na_2O. The difference is of more importance than might at first thought, be supposed, since the strength of the alkali solution is based upon the figure determined empirically, and not upon the theoretical one. If the 23.2 proportion is wrong and twenty-three correct, a standard solution based upon the former ratio would give too low results in the proportion of 23.2 : 23.0. Thus a phosphate rock containing eighty per cent. calcium phosphate would appear, by such an analysis, to contain only 79.31 per cent.

It was decided, therefore, to repeat this part of the work, and in this re-examination the conditions were the same as those previously existing, except in one particular: the amount of phosphoric acid operated upon was smaller than that previously used. By referring to the original paper, it will be found that about eighty cubic centimeters of alkali were used in each of the titrations in question. This represents a quantity of the yellow precipitate much larger than would ever be obtained in the analysis of even the richest phosphate rocks; and in operating upon so large a precipitate the liability of error from incomplete washing is great. Any free acid remaining in the precipitate would, of course, result in too high a reading of the burette, with a corresponding error in the standardizing of the solution.

The following are the results obtained in this re-examination:

Some di-sodium hydrogen phosphate, bought as chemically pure, was dissolved in hot distilled water, filtered, and crystallized; the crystals were washed, dissolved again in water, and recrystallized. Of the resulting crop of crystals, about forty-five grams were dissolved in one-half liter of water. The strength of this solution was then determined.

	Weight of Na_2HPO_4 solution, grams.	Grams.	
I	20.0814	gave 0.7581	$Na_4P_2O_7$
II	17.9585	gave 0.6778	$Na_4P_2O_7$
III	36.9115	gave 1.1652	$Mg_2P_2O_7$

The magnesium-ammonium phosphate precipitate was filtered, dissolved in acid and reprecipitated by ammonia.

By a coincidence each of these three determinations gave precisely the same result; *viz.*,

TABLE I.

	Grams P_2O_5 in 10 grams of solution.
I	= 0.2014
II	= 0.2014
III	= 0.2014

Therefore, ten grams of the sodium phosphate solution contained 0.2014 grams P_2O_5.

Weighed portions of this same solution were now precipitated by ammonium molybdate, thoroughly washed and titrated. The results are given in Table II.

TABLE II.

I.	II. Grams Na_2HPO_4 solution taken.	III. Equivalent to grams P_2O_5.	IV. cc. of KHO solution used.
A	2.0410	0.04110	41.05
B	2.3710	0.04775	47.70
C	2.2920	0.04616	46.20
D	2.4690	0.04972	49.60

Dividing the figures in Column III by those in Column IV, and multiplying the result by 100, we obtain the number of milligrams corresponding to 100 cubic centimeters of the potassium hydroxide solution, as follows:

TABLE III.

	Mgms. P_2O_5.
A	= 100.12
B	= 100.11
C	= 99.91
D	= 100.24
Average	= 100.09

Therefore, 100 cubic centimeters of the potassium hydroxide

solution neutralize an amount of the yellow precipitate corresponding to 100.09 milligrams of P_2O_5.

The standard acid was now titrated against the standard alkali, using phenolphthalein as the indicator, whereby the two solutions were found to be of exactly equal strength.

The standard acid was then titrated against pure sodium carbonate, using phenolphthalein at boiling heat:

	Grams Na_2CO_3 used.	cc. of acid used.	100 cc. acid equal to mgms. Na_2CO_3.
I	0.9099	52.95	1719
II	0.9168	53.35	1719

Therefore, 100 cubic centimeters of acid are equivalent to 1719 milligrams sodium carbonate, and since the alkali solution is of the same strength as the acid, 100 cubic centimeters of it also are equivalent to 1719 milligrams sodium carbonate.

As we have already seen, by Table III, that 100 cubic centimeters of the alkali are required to neutralize 100.09 milligrams of P_2O_5 (in the form of ammonium phosphomolybdate), it follows that 1719 milligrams sodium carbonate are required for 100.09 milligrams P_2O_5.

Dividing each by its molecular weight we have

$$\text{for } P_2O_5 \ \frac{100.09}{142.06} = 0.7045$$

$$\text{for } Na_2CO_3 \ \frac{1719.0}{106.1} = 16.20$$

Therefore,

$$P_2O_5 : Na_2CO_3 = 0.7045 : 16.20 = 1 : 22.99$$

In other words, 23 molecules of sodium carbonate (or of Na_2O) are required to neutralize the yellow precipitate containing one molecule of P_2O_5, and the former figure (that given in my paper of last autumn) 23.2 molecules, is incorrect.

Referring to Table II of the present paper, it may be stated that in analysis A the yellow precipitate was washed on an ordinary filter without using suction, the precipitate being washed on the filter, transferred to the beaker and then again filtered and washed. In analysis B, of the same table, the precipitate was washed on the ordinary filter, with the aid of the suction pump. In analyses C and D, the precipitates were washed with suction on a porcelain funnel with a fixed perforated plate in it.

This form of funnel is known as the Hirsch funnel.[1]

As in all cases the results were nearly identical; it is evident that the different methods of washing the precipitate had no influence upon the result. Exactly twenty-three molecules of Na_2O are required for one molecule of P_2O_5. The standard acid is prepared by diluting 323.7 cubic centimeters of normal sulphuric acid to one liter, and not 326.5 cubic centimeters as previously stated. The alkali solution, after removing carbon dioxide by barium hydroxide, is brought to the same strength as the acid, volume for volume.

One cubic centimeter of either solution is then equal to one milligram of P_2O_5.

PHILADELPHIA, PA., February 20, 1894.

NOTE ON PEMBERTON'S METHOD OF PHOSPHORIC ACID DETERMINATION AS COMPARED WITH THE OFFICIAL METHODS.[2]

BY WM. C. DAY AND A. P. BRYANT.

HAVING occasion to make a series of determinations of phosphoric acid in Florida phosphate rock, we have used the method recently described by Mr. H. Pemberton, Jr., and incidentally have made a number of comparisons between it and the official method. The following are the results:

GRAVIMETRIC DETERMINATIONS.

No. 1. From 0.7867 gram $Na_2HPO_4 + 12H_2O$, obtained 0.2426 gram $Mg_2P_2O_7$

No. 1. From 1.1100 grams $Na_2HPO_4 + 12H_2O$, obtained 0.3433 gram $Mg_2P_2O_7$

No. 2. From 1.0000 gram Florida rock, obtained 0.5828 gram $Mg_2P_2O_7$

No. 3. From 0.3807 gram Florida rock, obtained 0.0262 gram $Mg_2P_2O_7$

No. 3. From 0.4831 gram Florida rock, obtained 0.0333 gram $Mg_2P_2O_7$

No. 4. From 1.0036 grams Florida rock, obtained 0.0227 gram $Mg_2P_2O_7$

[1] To be had from Bullock and Crenshaw, Philadelphia. A disk of filter paper of the diameter of an American silver quarter dollar (fifteen-sixteenths inch) is used, when employing the smallest size funnel. I can highly recommend this funnel in all cases in which the precipitate is to be titrated. The precipitate presents a perfectly flat surface, is easily and quickly washed, and is readily transferred with the aid of the wash bottle to the beaker. The funnel can be employed only when using the suction pump, but it has the advantage of not requiring a platinum cone, and the size of the filter is reduced to a minimum.

[2] Read at the stated meeting of the Chemical Section, of the Franklin Institute held February 20, 1894.

DETERMINATIONS BY PEMBERTON'S METHOD.

No. 1 used 1.0737 grams $Na_2HPO_4 + 12H_2O$ and 22.88 cubic centimeters KOH solution and 1.85 cubic centimeters acid.

No. 1 used 1.0370 grams $Na_2HPO_4 + 12H_2O$ and 21.30 cubic centimeters KOH solution and 0.80 cubic centimeter acid.

No. 2 used 1.0000 gram Florida rock and 41.85 cubic centimeters KOH and 5.05 cubic centimeters acid.

No. 3 used 1.0000 gram Florida rock and 7.55 cubic centimeters KOH and 3.10 cubic centimeters acid.

No. 4 used 1.0000 Florida rock and 6.75 cubic centimeters KOH and 5.50 cubic centimeters acid.

Strength of H_2SO_4 used 1 cubic centimeter = 0.015998 gram H_2SO_4.

Strength of potassium hydroxide solution 1 cubic centimeter = 0.01847 KOH.

The percentages of P_2O_5, calculated from the foregoing determinations, are:

Substance.	Gravimetric.	Pemberton.
No. 1, sodium hydrogen phosphate	19.72	19.73
No. 1, sodium hydrogen phosphate	19.78	19.99
No. 2, Florida rock	37.28	37.22
No. 3, Florida rock	4.40	4.53
No. 3, Florida rock	4.41	...
No. 4, Florida rock	1.45	1.32

It is evident from the above figures that the agreement between the results of the two methods is as close as could be desired. Inasmuch as the Pemberton method is of extreme accuracy, is very easily carried out and effects a great saving of time and labor over the official method, it is well worthy of extended use. We have found that the author's statement of the time required for a single determination, namely, thirty to forty minutes from the time the solution is measured out for titration, is entirely reasonable. Omitting filtration of silica makes no difference in the accuracy of the results.

SWARTHMORE COLLEGE, PA., February 20, 1894.

THE CHEMICAL AND PHYSICAL EXAMINATION OF PORTLAND CEMENT.

(*Continued from Page 273.*)

BY THOMAS B. STILLMAN, PH.D.

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of sand, 319, 320. Effect of modifying the present test for cement, and adding one for fineness and specific gravity, 324. Time allowed for setting regulated according to quantity of water used, 317. Deterioration of cement during a voyage to Bombay, 318.

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[TO BE CONTINUED.]

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

SUB-COMMITTEE ON METHODS.[1]

BULLETIN No. 2.

CIRCULAR TO IRON AND STEEL CHEMISTS ON METHOD OF DETERMINING PHOSPHORUS.

AT the World's Congress of Chemists in Chicago a Sub-Committee of the original Committee on International Standards for the Analysis of Iron and Steel was appointed to

[1] The Sub-Committee on Methods for the Analysis of Iron and Steel, have sent the following bulletin to the iron and steel chemists of the country, so far as they could get their names. They earnestly request that any who do not receive a copy of the circular, but who do see this, will comply with the request of the bulletin, the same as though they had received a circular direct.

consider the subject of Standard Methods.

This sub-committee consists of Dr. C. B. Dudley, Chairman, Messrs. A. A. Blair, W. P. Barba, P. W. Shimer, and T. M. Drown. It has recently held a meeting and has decided to recommend standard methods in iron and steel analysis to be used as the basis of commercial transactions. The sub-committee fully appreciates the fact that these methods, to have the highest value, should be in facility and in time of execution such that they will readily recommend themselves for daily use in iron and steel works.

To further this end the sub-committee wishes to have the co-operation of the iron and steel chemists of the country, and to ask them for a brief outline of the processes or methods they use and prefer for the determination of different elements in iron and steel, and for such other information and suggestions as they think will aid it in the work before it. The sub-committee recognizes the fact that it will add immensely to its efficiency and value if the iron and steel analysts of the country will take a personal interest in it, and aid it by their counsel and active influence.

You are therefore requested to send to the chairman of the sub-committee, as soon as convenient, such an outline as you may deem sufficient to fully describe your practice. It is suggested that you follow the general plan here indicated, by answering the following questions, which may be referred to by number to save you unnecessary trouble:

First. What general method do you use for the determination of phosphorus in iron and steel?

Second. What special precautions do you consider necessary to make this method reliable?

Third. What precautions do you take to prevent the interference of arsenic?

Fourth. What factors do you use in your calculations?

Fifth. What variations do you introduce in the case of iron ores or slags?

Sixth. Do you use the same method in pig iron and steel and do you consider the results equally reliable?

Seventh. Do you ever examine the residues insoluble in acid,

in pig irons, or iron ores, and do you ever find phosphorus in them?

Eighth. Are all your determinations made by the same method, or do you check your work by reference to another method, and if so, what method do you use for this purpose?

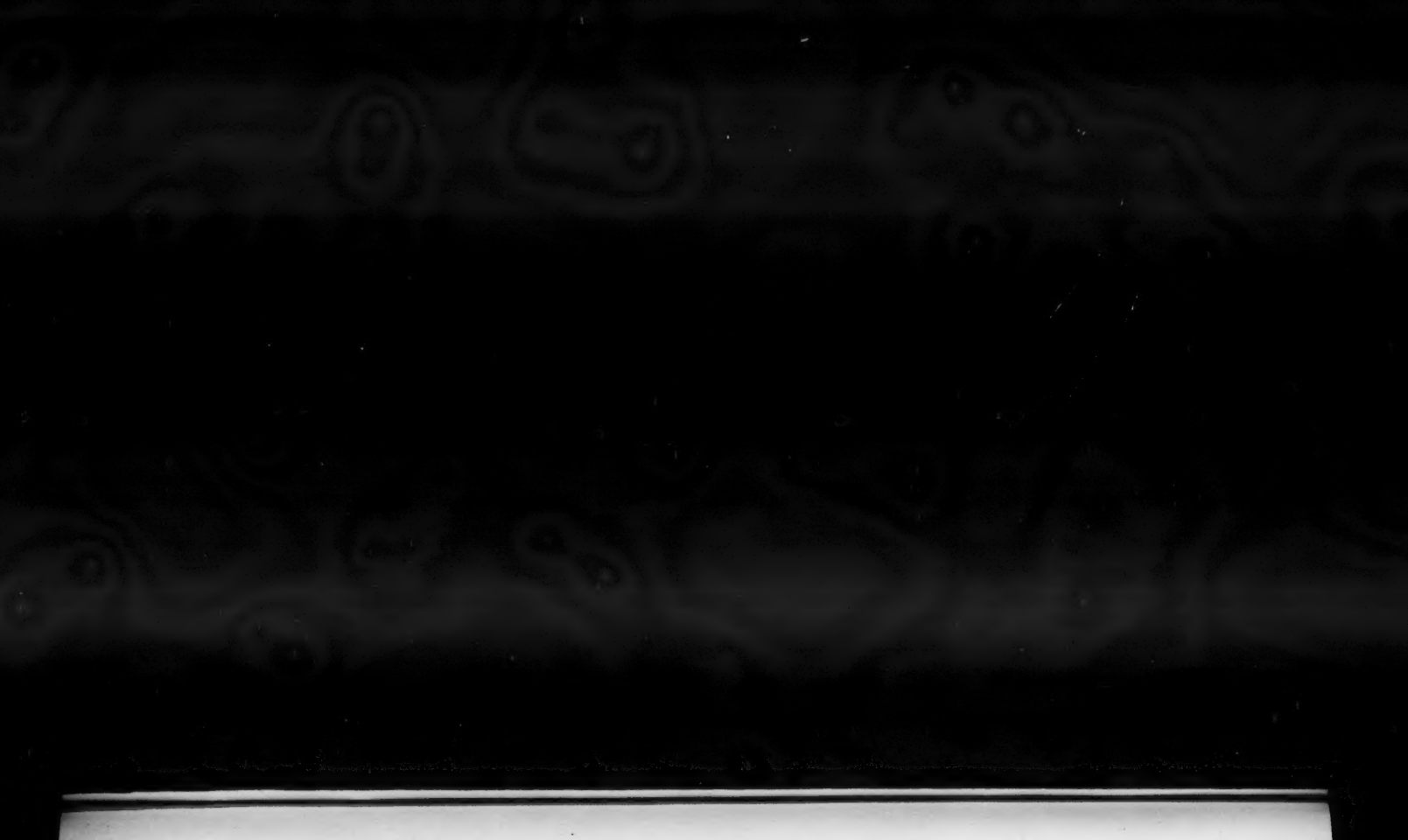
Ninth. How many determinations do you make a day in your laboratory under ordinary circumstances?

Tenth. What do you consider the greatest length of time necessary to obtain a result, permissible in your work?

The sub-committee begs that you will send at the earliest possible moment as full replies to all or any of the above questions as you conveniently can, and assures you that in making use of any details that may be original with you, you shall have full credit. You will likewise be furnished with copies of the various reports.

CHAS. B. DUDLEY,
Chairman Sub-Committee,
ALTOONA, PA.

APPROVED,
J. W. LANGLEY,
Chairman Com. on Int. Standards.

ERRATUM.

In the column showing percentages for the No. 2 steel on page 219 this number, *0.041* should read *0.048*.